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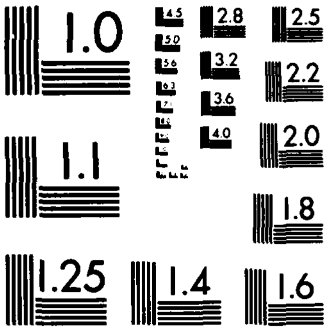

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ABSTRACT

This thesis describes some of the chemistry of copper(II) heteropolyoxotungstate anions viewed as inorganic analogues of copper porphyrins.

The heteropolytungstate anions, $[XW_{11}O_{39}Cu(II)\text{-}OH_2]^{n-}$ (X = Si, B, Zn) were synthesized and isolated as the potassium salts. Electrochemical investigation of these anions at pH 2.2, 4.7, and 6.0 revealed no evidence of oxidation to Cu(III) derivatives. Organic solutions of the Si heteropolyanion were generated by extracting the aqueous potassium salt into benzene and toluene using tetraheptylammonium bromide. The $(Bu_4N)_4H_2SiW_{11}O_{39}Cu$ (I) salt (soluble in acetonitrile) was isolated and characterized by analysis, potentiometric titration and ESR spectroscopy.

In the polar and nonpolar non-aqueous solvents, the water molecule coordinated to the Cu is lost, as shown by changes in ESR and optical spectra. Cyclic voltammograms of I and its deprotonated form (II) in acetonitrile showed no copper oxidation feature. Treatment of solutions of II in toluene or acetonitrile with Br_2 or O_2 at ambient and low temperatures did not result in oxidation or oxygen-

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ation of the heteropolyanion. Corresponding treatment with superoxide anion, O_2^-, led to new ESR-active products.

GEORGETOWN UNIVERSITY
GRADUATE SCHOOL

The dissertation of Capt. Christine M. Kelly entitled

Electrochemical and Spectroscopic Studies of Some Tungstocuprate Heteropolyanions in Polar and Nonpolar Solvents. Reaction with Superoxide.

submitted to the department of Chemistry in partial fulfillment of the requirements for the degree of Master of Science in the Graduate School of Georgetown University has been read and approved by the Committee:

Michael Pope

Louis C.W. Baker

Joseph E. Earley

Head of Department

March 25, 1986

Date

ELECTROCHEMICAL AND SPECTROSCOPIC STUDIES OF SOME TUNGSTOCUPRATE HETEROPOLYANIONS IN POLAR AND NONPOLAR SOLVENTS. REACTION WITH SUPEROXIDE.

A Thesis
submitted to the Faculty of the
Graduate School of Georgetown University
in partial fulfillment of the requirements for the
degree of
Master of Science

By

Christine M. Kelly, Capt, USAF
Miami University, Oxford, Ohio, (1977) B.S.

Washington, DC
March, 1986

Dedicated to my husband and son

Darby J. Kelly, Major, USAF

S. Michael Kelly

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LIST OF FORMULA ABBREVIATIONS

$[SiW_{11}O_{39}Cu(II)]^{6-}$	$[SiW_{11}Cu(II)]^{6-}$
$[BW_{11}O_{39}Cu(II)]^{7-}$	$[BW_{11}Cu(II)]^{7-}$
$[ZnW_{11}O_{39}Cu(II)]^{8-}$	$[ZnW_{11}Cu(II)]^{8-}$
$(CH_3CH_2CH_2CH_2)_4N^+$	TBA
$(CH_3(CH_2)_6)_4N^+Br$	THpAB
CH_3COOH	HOAc
CH_3COO^-	OAc^-

CHAPTER I

INTRODUCTION

This thesis presents the chemistry of some copper polynuclear oxometalate complexes, often refered to as heteropolyanions. An extensive review of heteropolyanions is found elsewhere[1] and this thesis will be limited to some copper derivatives of the Si, B, and Zn polyoxotungstates. These substituted heteropolyanions are derivatives of structures known as Keggin anions. The structure of the Keggin complexes is described as follows. Three edge shared MO_6 octahedra form an M_3O_{13} triad; four triads are then joined through shared corners to each other and to the central XO_4 tetrahedron. The Keggin structure, $[XM_{12}O_{40}]^{n-}$, is depicted in Figure 1. The loss of one $[WO]^{4+}$ unit from a triad creates a vacancy and occurs on treatment of the Keggin structure with alkali, resulting in structure B of Figure 1, known as a lacunary anion. Reconstruction of the Keggin structure from the lacunary anion can be accomplished by substituting a metal ion for the $[WO]^{4+}$ unit. Substituted Keggin anions of this type were first reported by Baker et al.[2] and were

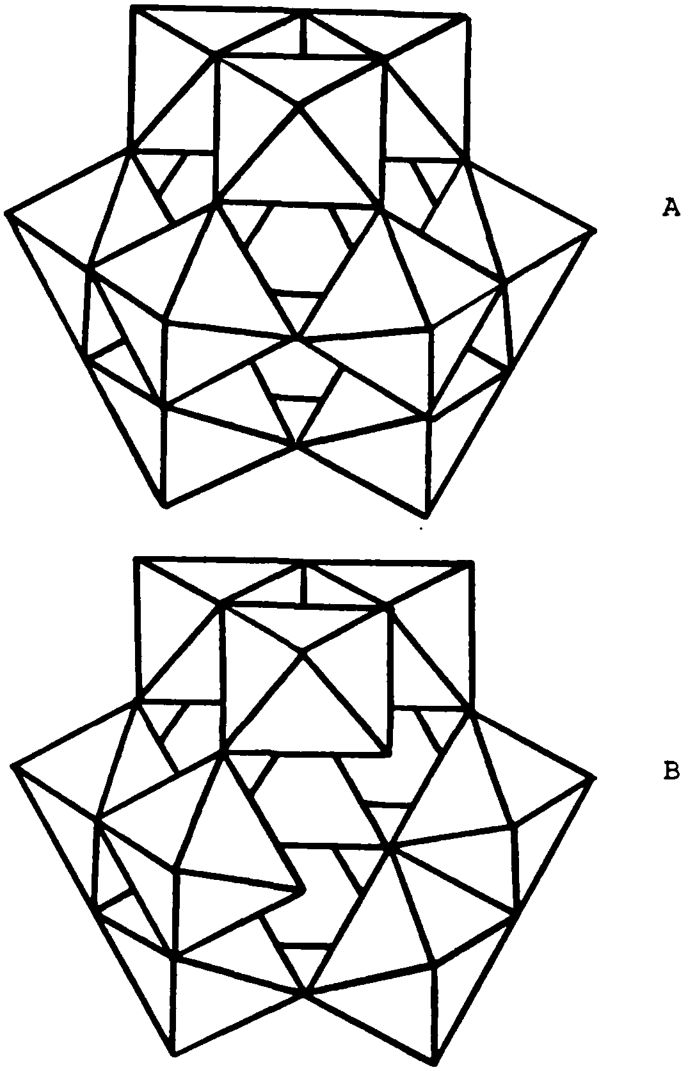

Figure 1: Polyhedral representations of (A) $\alpha\text{-}XW_{12}O_{40}{}^{n-}$ and (B) $\alpha\text{-}XW_{11}O_{39}{}^{(n+4)-}$

prepared by direct synthesis, i. e. without the prior isolation of a lacunary anion. Subsequently, the lacunary anions were synthesized by acidification of stoichiometric quantities of the XO_4^{m-} and tungstate solutions and the products were reacted with appropriate metal ions[3]. The complexes investigated in this research are formed by this direct method and are:

$$[SiW_{11}O_{39}Cu(II)\text{-}OH_2]^{6-}$$
$$[BW_{11}O_{39}Cu(II)\text{-}OH_2]^{7-}$$
$$[ZnW_{11}O_{39}Cu(II)\text{-}OH_2]^{8-}$$

where X, the heteroatom of the central tetrahedron, is Si, B, or Zn; M, the addenda atoms of the MO_4 groups, are Ws; and copper(II) fills the lacunary position.

As seen in Figure 2, the copper(II) is apparently 6-coordinate and has essentially two ligands: 1) a pentadentate ligand with a Cu-O bond to the central tetrahedron and four W-O-Cu bonds; and 2) a monodentate ligand (water) occupying copper's remaining unshared co-ordination position. It has been argued, based on the IR spectrum of $[PW_{11}O_{39}Cu(OH_2)]^{5-}$, that the Cu-O(P) bond is of low bond order and that in this compound, at least, the Cu should be regarded as 5-coordinate[4]. Copper(II) has a

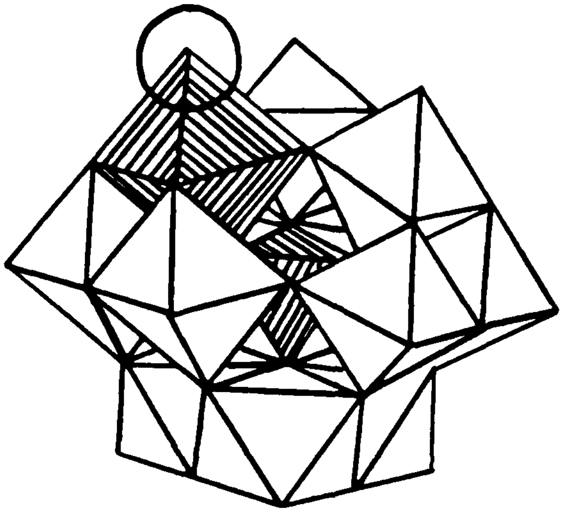

Figure 2: The substituted lacunary, $XW_{11}Cu(II)$ showing copper as the shaded outer octahedron. The circle indicates the position of the fifth ligand.

d^9 configuration and with a coordination number of 5, readily adopts a square-based pyramidal geometry[5.a].

Baker and Figgis[6] demonstrated that with Co(II) and Co(III)SiW_{11} complexes the coordinated water molecule could be replaced with NH_3 or pyridine. Katsoulis has shown[7] that extraction of $[SiW_{11}O_{39}Cu\text{-}OH_2]^{6-}$ into nonpolar solvents removes the water molecule and that pyridine can become coordinated to the copper. In the nonpolar solution, where the water molecule has been removed, the copper is now essentially four-coordinate and in a nearly square-planar environment. The ligand-on/ligand-off behavior is supported by spectroscopic evidence. Katsoulis reports[7] near-IR absorption data and ESR coupling parameters for $SiW_{11}Cu(II)$ complexes. In aqueous solution, where H_2O is the fifth ligand, the near-IR absorption occurs at 875 nm; but in toluene with the water molecule ligand off, the absorption shifts to 710 nm. The ESR $A_{\parallel}$ value increases from 90 G for the $SiW_{11}Cu(II)\text{-}OH_2$ complex in water to 120 G for the same complex in toluene. Katsoulis demonstrated the regeneration of a ligand-on complex in toluene by adding excess pyridine; the near-IR absorption and the ESR parameters returned to those of the ligand-on values. Thus ligand-on/ligand-off conditions can be ascertained from near-IR and ESR spectroscopic measurements.

Both the near-IR absorbance values and ESR $A_{\parallel}$ values are sensitive to the site stereochemistry at the copper atom. The electronic transitions occuring in this energy region are d-d transitions of the copper electrons. The relative ordering of the d orbitals, and hence the energy of the transition is very sensitive to the stereochemistry of the copper[8]. Briefly summarizing the findings in Reference 7, in the presence of an axial fifth ligand on Cu(II), the site symmetry is C_{4V}. When the ligand is removed, the symmetry becomes D_{4h} and the splitting between d_{xy} and d_{z^2} orbitals increases. Thus in the absence of a fifth ligand on copper, the transitions between these two orbitals are of greater energy than when the ligand is present, and the transitions occur at shorter wavelengths. For the $SiW_{11}Cu(II)$ complexes, the color of the solution reflects the environment of the copper: aqueous solutions (ligand-on) are colorless and organic solutions (ligand-off) are aqua (pale blue-green).

Likewise the $A_{\parallel}$ values in the ESR spectra are sensitive to the stereochemistry at the copper site. In the presence of the axial ligand, the $A_{\parallel}$ value is less than that in the absence of the ligand.

In addition to binding small ligand molecules such as H_2O, NH_3, and pyridine, the metal in the lacunary position can undergo electron transfer reactions. For example, Mn(II) in $[SiW_{11}Mn(II)]^{6-}$ can be oxidized to Mn(III) with either Br_2[9] or O_2[10]. Iron complexes, such as $SiW_{11}Fe(II)$[11] are also rapidly oxidized upon exposure to atmospheric oxygen. It therefore appeared possible that copper might also exhibit such redox behavior in the heteropolytungstates.

In many respects the substituted Keggin anions, especially in their ligand-off forms, might be expected to resemble macrocylic metal complexes like the metalloporphyrins. Katsoulis has, for example, demonstrated O_2 binding by some Mn(II) polytungstates[7]. It therefore appeared possible that Cu(II) in the heteropolyanions might exhibit chemical behavior similiar to that of Cu(II) in biological molecules. Copper plays a key role in many biological enzymes[12, 13.a, 14.a]. In biological systems, copper (in addition to other metals) is found in metalloenzymes[15] and functions in the transportation of oxygen and its metabolism, the transfer of electrons, and the insertion of dioxygen into other molecules[12, 13.a, 16]. An example of these functions is the superoxide dismutase (SOD)[15] enzyme which catalyzes the disproportionation of the superoxide dianion, O_2^-. Copper in hemocyanins[13.a] acts as an oxygen carrier while copper salts catalyze the oxygenation of organic substrates by iodosylbenzene[16, 17]. Thus, in biological and other organic reactions copper reacts with O_2 and O_2^-. It appeared probable that this reactivity toward oxygen, and possibly other ligands, might be duplicated in the copper heteropolyanion.

In biological systems, Cu(I), Cu(II), and Cu(III) are readily attainable oxidation states[14.b]. Copper(I) in cytochrome oxidase, the terminal enzyme of cellular respiration, transfers electrons to molecular oxygen[13.b]. Copper(III), usually thought of as an usual high oxidation state, is quite common in biological systems[14.c]. It is stabilized by coordination to peptides[18.a], and the resulting complexes have relatively long life times in aqueous solutions[18.b]. Therefore, it was felt that copper(III) might be an attainable oxidation state in a heteropolyanion.

The purpose of this research was to determine if copper heteropolyanions would exhibit similiar chemistry to that of other metals in heteropolyanions and to that of copper in biological systems; that is, bind small ligand molecules and become oxidized or reduced to other states.

CHAPTER II

EXPERIMENTAL

A. Vibrational Spectra

Infrared spectra were recorded on a Unicam Model 3-100 grating infrared spectrophotometer. Solid samples were recorded using KBr pellets ("IR Grade" from Fisher Scientific Co.) The pellet was made using a metal mini press, which also served as the sample holder in taking the spectrum.

B. Electronic Spectra

For spectra in the near infrared region (600 nm - 1200 nm) characteristic of the copper (II) absorption, the Cary 14, a dual beam spectrophotometer, was used. Matched quartz cells were employed (Scientific Cell Co. and NSG Precision Cell, Inc.) with path lengths of 1.0 cm and 0.10 cm. For all O_2^- samples the HP 8451 spectrophotometer and the 0.10 cm cells were used to allow for rapid scans and to avoid photodecompostion.

C. Electrochemistry

1) Cyclic Voltammetry

For the aqueous solutions of the potassium salts of Si, B, and Zn copper(II) polyoxotungstates the cyclic voltammograms were obtained in three different pH buffers. Concentrations were approximately 0.01M in each of the buffers. For the 5 x 10^{-3} M solutions of the tetra-n-butylammonium (TBA) salts of $[SiW_{11}Cu(II)]^{6-}$ in CH_3CN, the cyclic voltammograms were recorded using 0.1 M TBA in CH_3CN as the supporting electrolyte.

All cyclic voltammograms were recorded in a polarographic cell (Metrohm EA 875-50) using a glassy carbon electrode (Princeton Applied Research 9333) as the working electrode. The reference electrode was a saturated calomel electrode (SCE) and a platinum wire served as the counter electrode. Each sample was purged with nitrogen prior to analysis. Since ordinary tank nitrogen contains oxygen, it was necessary to treat the nitrogen prior to its use. For aqueous sample solutions the nitrogen was passed through a scrubbing tower (containing a vanadous chloride scrubbing solution) and another tower containg deionized water before purging the solutions. However, for organic solutions, the nitrogen gas was passed through two columns to ensure not only deoxygenation but also dryness. The first column, connected to a heater, was filled with BASF catalyst and the other column contained a molecular sieve Type 4A desiccant. Nitrogen passed through these columns was then used to purge the non-aqueous solutions.

For recording the voltammogram, a combination of Mckee-Pederson Modules (MP 1006C, MP 1008B, MP 1009A, MP 1012, MP 1031, MP 1032, and MP 1042) interfaced to an Omnigraphic 2000 (Houston Instruments, Hewlett Packard Model No. 7035B) X-Y recorder was used.

2) Controlled Potential Electrolysis

Electrolytic reduction of the copper in the heteropoly anions was carried out using a Brinkman Wenking Potentiostat (Model 70 TST) and a Koslow Scientific Company digital coulometer (Model 541). The electrolysis cell contained a 5×10^{-3} M solution in 1.0 M acetate buffer (pH = 4.7) and a graphite cloth (Union Carbide Corporation, x 2010) as the working electrode. A silver/silver chloride electrode (IBM Instruments, Inc.) served as the reference electrode. The anode compartment was connected to the cathode compartment by a fritted disc and contained a platinum wire immersed in the same acetate buffer solution. These aqueous solutions were purged with nitrogen as described in Section C.1.

For the organic solutions of $[SiW_{11}Cu(II)]^{6-}$ in CH_3CN, the same setup was used. A 3.5 x 10^{-3} M $[SiW_{11}Cu(II)]^{6-}$ CH_3CN solution with 0.1 M $TBAClO_4$ as the supporting electroyte was electrolyzed; the anode compartment contained 0.1M $TBAClO_4$ in CH_3CN. Purging was accomplished using the dry nitrogen described previously; the dried nitrogen passed through an acetonitrile bubbler prior to entering the electrolysis cell to prevent loss of solvent during the electrolysis.

D. pH and Electrical Potential Measurements

All pH and electrical potential measurements were done on a Fisher Accument Model 220 pH meter. The electrode was a Sensore combination pH electrode. Certified buffers (Fisher Scientific Co.) were used to standardize the pH meter.

The potentiometric titration of the protonated TBA salt of $[SiW_{11}Cu(II)]^{6-}$ with standardized TBAOH (Aldrich Chemical Company) was accomplished by the following general procedure. The solution to be titrated was placed in a 20 mL beaker equipped with a combination pH electrode and a stirrer. Aliquots of TBAOH were added using a microliter pipette (Kainin, capable of delivering up to 20 μL aliquots in 0.1 μL additions). The solution was stirred and the stabilized mV reading recorded. Titration curves of TBAOH volume versus mV were made; the end point was read from the curve. In the heteropolyanion titrations the potential reading was less stable upon addition of base exceeding the second end point.

TBAOH was standardized against potassium hydrogen phthalate (KHP, Thorn Smith). An approximately 0.1 M TBAOH solution was prepared by diluting reagent TBAOH (25% in methanol, 59.4 mL) with 500 mL CH_3CN. KHP samples were weighed (ca. 20 mg) and dissolved in 50 mL H_2O. Ten mililiter aliquots of solution were pipetted into a 20 mL beaker as described above. TBAOH was added by microliter pipette and the mV reading recorded. Titration curves were made and the volume of base required for the endpoint determined. Three separate titrations were used to find the TBAOH molarity of 0.212 M. This standardized TBAOH was then used to titrate the TBA salts of the protonated $[SiW_{11}Cu(II)]^{6-}$ anions.

E. Electron Spin Resonance

X-band ESR measurements were made on a Varian E-4 spectrometer, equiped with a TM_{110} rectangular cavity. All spectra were obtained at liquid nitrogen temperatures (LN_2, 77 K) using standard quartz sample cells in an immersion Dewar filled with liguid nitrogen; gaseous nitrogen was continuously passed through the cavity to keep it free of condensed water. Aqueous samples were approximately 5 x 10^{-3} M solutions of the heteropolyanion in aqueous glycerol (1:1). The external standard was the DPPH radical (g = 2.0037). Computer simulations of these spectra were made using the computer program, PROGRAM CURHEPR (program is described in Reference 19).

CHAPTER III

RESULTS AND DISCUSSION

1. Preparation of Copper(II) Heteropolyanions in both Aqueous and Non-Aqueous Solvents

The synthesis of the heteropolyoxotungstates in both solvents followed reported methods. For the synthesis of the potassium heteropolyoxotungstocuprates, a slight modification of reported methods was devised. The usual synthesis method for the tungstosilicocuprate anion involves isolation of the lacunary and subsequent conversion to the copper(II) compound by reaction with $CuSO_4$ or $Cu(NO_3)_2$[3]. Due to low yields of the boron and zinc $[XW_{11}O_{39}]^{n-}$, the reported method is a direct synthesis from starting materials to the final copper compound without isolating the intermediate anion. In this research, a direct synthesis method for the copper (II) tungstosilicates was devised and pure compounds were obtained without isolating the lacunary tungstosilicates.

To generate solutions of the tungstosilicocuprate anion in organic solvents, two methods were used. To make solutions in toluene or benzene, a given volume of aqueous solution of the potassium salt of the heteropolyanion was extracted using an equal volume of the organic solvent containg a phase transfer agent (THpAB). Since the charge on the heteropolyanion is 6^-, a 6-fold excess of the transfer agent was used. This method of extraction is thoroughly described by Katsoulis[7].

For acetonitrile solutions, the TBA salt of the $[SiW_{11}Cu(II)]^{6-}$ anion was precipitated from the aqueous solution of the potassium salt of the anion and dissolved in CH_3CN.

A. Reagents and Materials

Materials and solvents used were as follows.

1) Starting Materials

From J.T.Baker Chemical Co, Baker Analyzed Reagents; sodium tungstate-dihydrate, sodium meta silicate-9-hydrate, cupric nitrate, zinc acetate, sodium sulfate, sulfuric acid, glacial acetic acid, sodium phosphate dibasic, sodium acetate trihydrate, acetonitrile, toluene and benzene.

From Fisher Scientific Co: boric acid (Certified A. C. S.) and bromine (Reagent A. C. S.).

From Alpha Products: dimethylsulfoxide (ultrapure) and tetra-n-butlyammonium bromide.

2) Buffers

Sulfate Buffer: 14.2 g Na_2SO_4 (0.1 mole) was dissolved in ca. 75 mL distilled H_2O. H_2SO_4 then added to decrease pH to 2.0. Then H_2O was added to bring volume to 100 mL.

Acetate Buffer: 136 g NaOAc (1.0 mole) was dissolved in 800 mL H_2O. The pH was decreased from 8.0 to 4.7 by adding approximately 100 mL acetic acid. The final volume was brought to 1 L by adding approximately 100 mL H_2O.

Phosphate Buffer: This was prepared by mixing two 0.2 M stock solutions: 1) $NaH_2PO_4-H_2O$ (Mallinckrodt Chemical Works, 2.78 g dissolved in 100 mL H_2O) and 2) $Na_2HPO_4-7H_2O$ (5.36 g in 100 mL H_2O). The pH was increased from 5.7 to 6.0 by addition of solid $Na_2HPO_4-7H_2O$.

3) Solvent Purification

Acetonitrile (CH_3CN) was dried by passing it through a column of Alumina Woelm N-Super (Woelm Pharma). The effluent was collected under argon and stored in the dry box (Vacuum Atmosphere Company).

Dimethylsulfoxide (DMSO) was dried by vacuum distillation over CaH_2 and stored in the dry box.

Toluene was dried by distillation from sodium benzophenone and stored in the dry box.

B. Synthesis of the Potassium Salts of Copper(II) Polyoxotungstate Anions in Water

1) Potassium α-undecatungstosilicocuprate

$$11\ WO^{2-}{}_4 + SiO_3{}^{2-} + Cu^{2+} + 16\ H^+ \ \mathrm{---->}$$
$$[SiW_{11}O_{39}Cu(II)\text{-}OH_2]^{6-} + 7\ H_2O$$

Based on the direct method reported by Tourne and Weakley[3], Na_2WO_4-$2H_2O$ (36.3 g, 0.11 mole) was dissolved in 150 mL H_2O. The pH was adjusted to 6.3 with 4 M HCl. Na_2SiO_3-$9H_2O$ (2.8 g, 0.01 mole) was added and the solution heated to 80-90° C with stirring. Saturated aqueous $Cu(NO_3)_2$ (2.5 g, 0.01 mole) was added dropwise with stirring to the tungstate solution; the solution turned from colorless to pale green. Excess KCl was added and the solution cooled overnight to allow crystal growth. Pale green crystals formed, were filtered off, washed and recrystalized from water. Product identification was made based on the infrared spectra (IR Fig 3) which matched the spectra reported by Thouvenot[4]. The near-IR spectra (Fig 4) agreed with that given by Tourne[3] for the salt $K_6SiCuW_{11}O_{40}H_2$-14 H_2O. Absorbance data are given in Table 1.

2) Potassium α-undecatungstoborocuprate

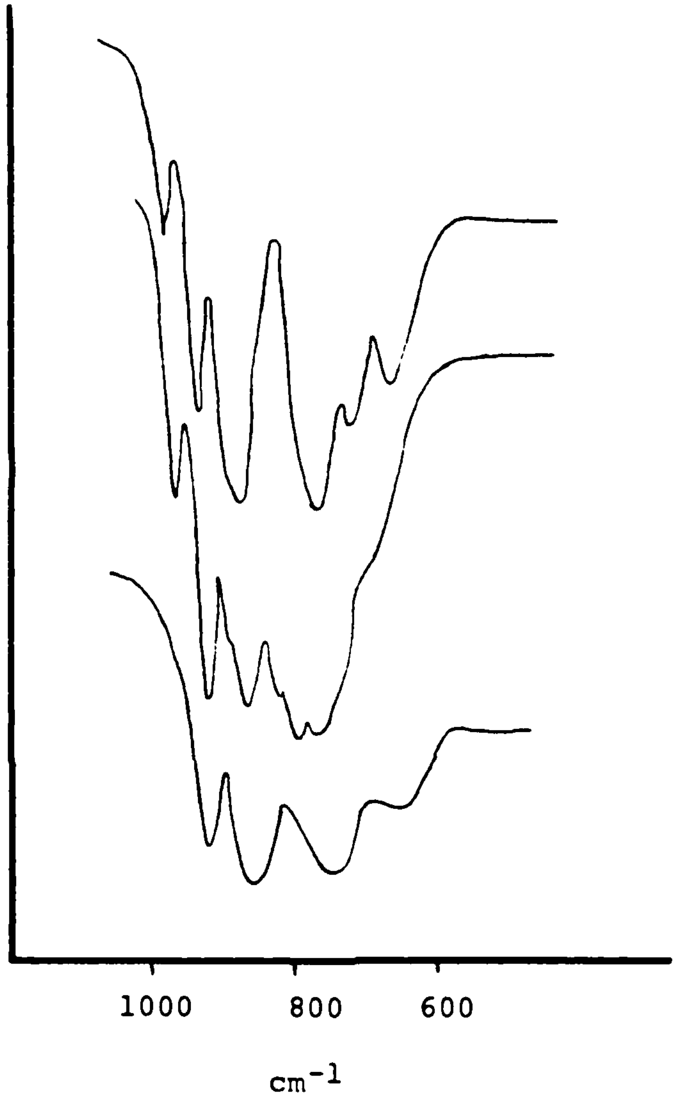

Figure 3: Infrared spectra of (A) $[SiW_{11}Cu(II)-OH_2]^{6-}$, (B) $[BW_{11}Cu(II)-OH_2]^{7-}$, and (C) $[ZnW_{11}Cu(II)-OH_2]^{8-}$ as K^+ salts in KBr

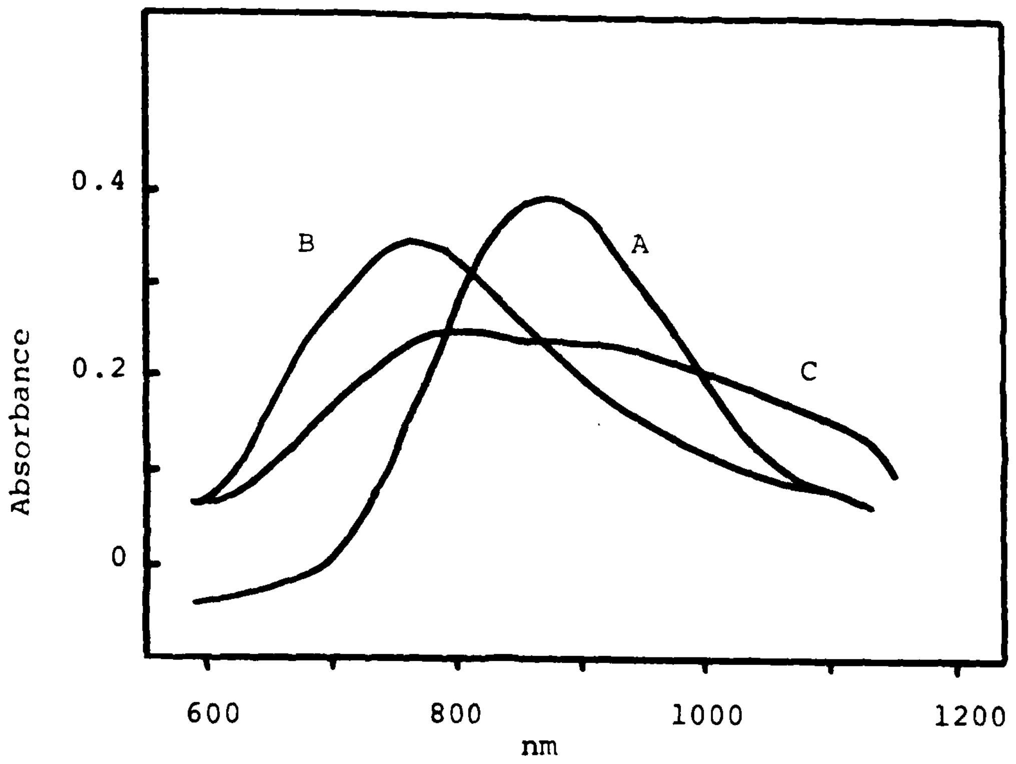

Figure 4: Near-Infrared absorption spectra of (A) $[SiW_{11}Cu(II)-OH_2]^{6-}$, (B) $[BW_{11}Cu(II)-OH_2]^{7-}$, and (C) $[ZnW_{11}Cu(II)-OH_2]^{8-}$ as K^+ salts in acetate buffer (pH = 4.7). (c = ca. 2×10^{-3} M; path length = 1 cm)

TABLE 1

Electronic Absorption Maxima of Cu(II) in Tungstate Anions as the K^+ Salts in Acetate Buffer

Near-IR Region

$[XW_{11}Cu(II)\text{-}OH_2]^{n-}$

X	Band (nm)	ε* (M^{-1} cm^{-1})
Si	875	43
B	765	23
Zn	790	20

* values reported by Tourne [3]

$$11\ WO^{2-}{}_4 + BO_3{}^{3-} + Cu^{2+} + 16\ H^+ \text{ ----> }$$
$$[BW_{11}O_{39}Cu(II)\text{-}OH_2]^{7-} + 7\ H_2O$$

The preparation followed the method reported by Tourne. Na_2WO_4-$2H_2O$ (36.3 g 0.11 mole) was dissolved in 150 mL H_2O. The pH was adjusted to 6.3 with glacial acetic acid. H_3BO_3 (2.5 g, 0.03 mole) was added and the solution heated to 80-90° C with stirring. Saturated aqueous $Cu(NO_3)_2$ was added as above; the solution turned from colorless to pale lime green. Excess KCl was added; the solution cooled overnight and pale green crystals were filtered off, washed and recrystalized from H_2O. Product identification was based on the IR (Fig 3) and the near-IR absorption of the copper (Fig 4). The near-IR spectra matched that given for $K_3Na_4BCuW_{11}O_{40}H_2$-17 H_2O.[3]

3) Potassium α-undecatungstozinccuprate

$$11\ WO^{-2}{}_4 + Zn^{2+} + Cu^{2+} + 16\ H^+ \text{ ----> }$$
$$[ZnW_{11}O_{39}Cu(II)\text{-}OH_2]^{8-} + 7\ H_2O$$

The preparation proceeded as reported above. Na_2WO_4-$2H_2O$ (36.3 g 0.11 mole) was dissolved in 150 mL H_2O. The pH was adjusted to 6.3 with glacial acetic acid.

$Zn(CH_3COO)_2$ (2.2 g, 0.01 mole) was added and the solution heated to 80-90° C while stirring. Saturated aqueous $Cu(NO_3)_2$ was added dropwise with stirring; the solution turned from colorless to aqua. Excess KCl was added; the solution cooled overnight and pale blue green crystals were filtered off, washed and recrystalized from H_2O. Again, product identification was based on the IR (Fig 3) and the near-IR spectra (Fig 4). This spectrum did not quite match that given by Tourne[3] and the product may be a mix of the copper heteropolyanion and free aquo Cu(II). The formula for the product given by Tourne is $K_7NaZnCuW_{11}O_{40}H_2$-14 H_2O.

C. Generation of the α-undecatungstosilicocuprate Salts in Non-Aqueous Solvents

1. Non-polar Solvents

a) Extraction into Toluene

Previously prepared $K_6SiW_{11}Cu(II)$ (0.8 g, 2.7×10^{-4} mole) was dissolved in 25 mL H_2O (1×10^{-2} M). The phase transfer agent was tetra-n-heptylammonium bromide (THpAB) and a 6×10^{-2} M solution was prepared (0.7 g THpAB, 1.4×10^{-3} mole dissolved in 25 mL toluene). The two colorless solutions were shaken in a 125 mL separatory funnel. A pale aqua organic layer immediately separated to the top. This color is indicative of the heteropoly anion in organic solutions when the water molecule (the fifth ligand on copper) has been removed. The organic layer was drawn off; the solvent removed via vacuum and the solid residue redissolved in dry toluene. The procedure was repeated three times and the final solution stored in the dry box.

b) Extraction in Benzene

Extraction into benzene proceeded exactly as above, substituting benzene for toluene. Drying of the solution was accomplished by bubbling dry N_2 through the solution for 2 hours prior to reaction.

2. Polar Solvents

a) Precipitation of the Tetra-n-butylammonium (TBA) Salt from Aqueous Solution

$(TBA)_4[H_2SiW_{11}O_{39}Cu(II)\text{-}OH_2]$

The polar solvent solutions of the polyoxotungstosilicatocuprate anions can be made by removing the non-polar solvent of the extracted heteropolyanion via vacuum and redissolving the dry residue in a polar solvent. Alternatively, the TBA salt can be precipitated from an acetate buffer solution of $[SiW_{11}Cu(II)-OH_2]^{6-}$ and redissolved in dry CH_3CN. Potassium undecatungstosilicocuprate (4 g, $1.2x10^{-3}$ moles) was dissolved in 30 mL acetate buffer (pH=4.7) and warmed to ca. 50° C. Saturated aqueous TBA bromide (3.8 g, $1.2x10^{-2}$ moles, dissolved in 2-3 mL H_2O) was added to the warmed buffer heteropoly solution. The solution immediately turned turbid pale blue. The solution was filtered to remove unreacted material and the pale blue precipitate was slurried with hot H_2O and refiltered. The precipitate was dissolved in 20 mL hot CH_3CN; ethyl acetate was added (3:1) to facilitate reprecipitation. The volume was reduced to ca. 15 mL by heating and the solution cooled (0° C) overnight. Pale blue crystals were filtered off and recrystalized from CH_3CN. Elemental analysis (E + R Microanalytical Laboratory, Inc., Corona, NY) gave 20.78% C, 3.87% H, and 1.60% N. Calculated for $(TBA)_4H_2SiW_{11}O_{39}Cu$: 20.71% C, 3.94% H, and 1.51% N. The presence of the two protons is supported by the titration results given below.

The above TBA salt was titrated potentiometrically with standardized TBAOH (M = 0.212) following the procedure described by Finke[20]. Sample 1 contained 187.8 mg and required 0.215(3) mL TBAOH (moles OH^-: moles H^+ = 0.90)

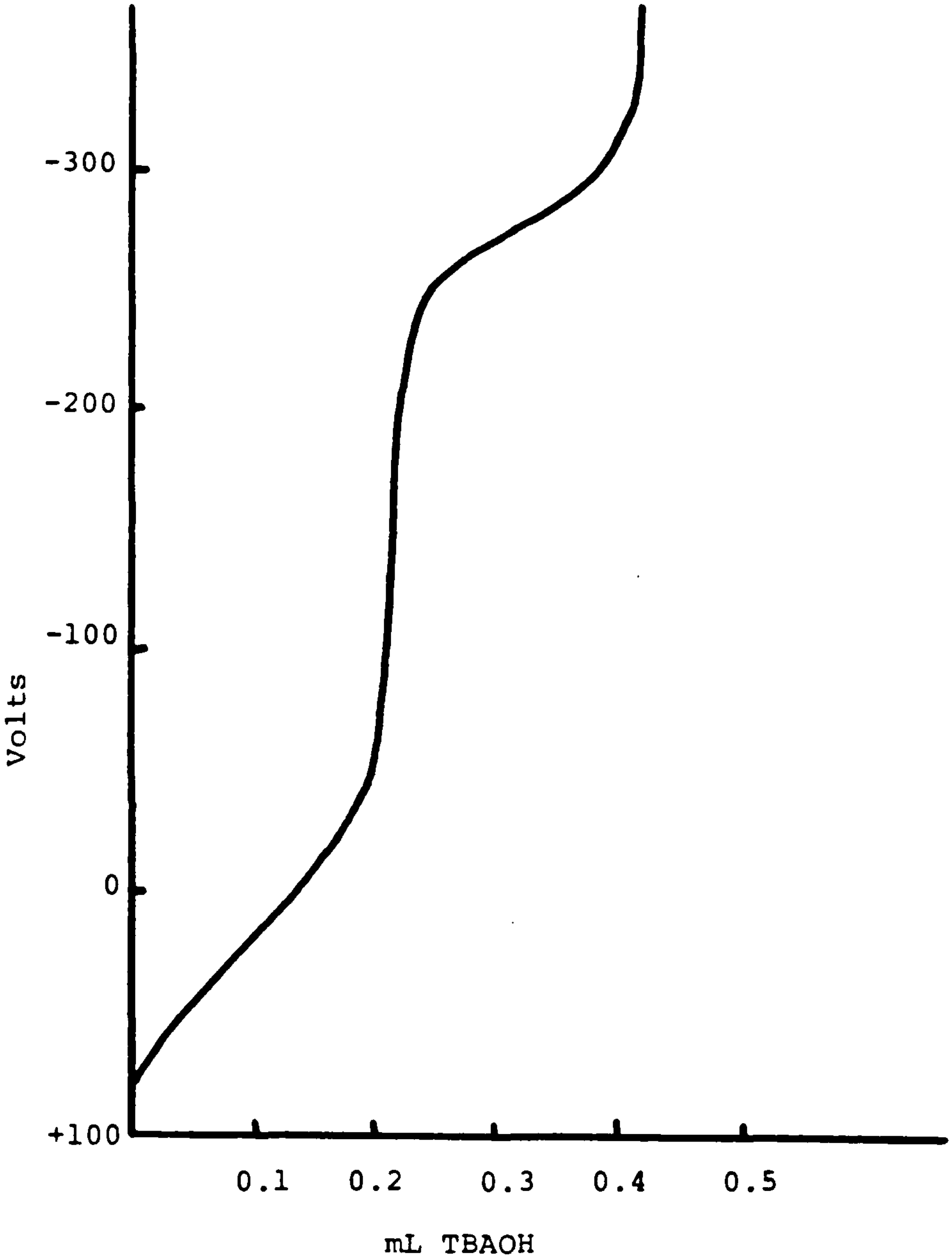

Figure 5: Potentiometric titration of 187.85 mg $[H_2SiW_{11}Cu(II)]^{4-}$ as the TBA salt with 0.212 M TBAOH in CH_3CN

to reach the first end point. The titration curve is shown in Fig 5. Although the second end point is clearly seen, the volume of base required is not accurately known due to the unstable mV reading at the end point. Sample 2 contained 184.9 mg of protonated heteropolyanion salt and required 0.220(3) mL TBAOH (moles OH^-: moles H^+ = 0.92) to reach the first equivalence point. Sources of error in this method of titration result from the filling and delivery of each aliquot of base from the pipette; the errors are cummulative and give a value of less than 1.0 for the ratio of base to protons. A large scale sample of 1.96 g in 50 mL CH_3CN was titrated; the solvent was removed via vacuum and the residue redissolved in dry CH_3CN. The drying procedure was repeated three times and the final dry solution stored in the dry box.

2. Aqueous Chemistry

A. Electrochemistry

The initial goal of this research was to determine if Cu(II) could be oxidized to Cu(III) in various $XW_{11}Cu(II)$ polyanions (X = Si, B, Zn). Knowing this oxidation would have a very high potential[14.c, 21], a stabilized Cu (III) heteropolyanion would probably be a very powerful oxidizing agent. As stated in the introduction, Cu(III) compounds are readily obtained species in biological systems; often the Cu(III) complex is stabilized by coordination to a peptide [18.a]. Similiarly, it was reasoned, a heteropolyanion might act to stabilize a Cu(III). The high negative charge of the heteropolyanion often stabilizes the metal in oxidation states that are normally unstable with respect to disproportionation, e.g. Mn (III)[1]. Thus, it seemed not unlikely that Cu(III) in a heteropolyanion might be stabilized.

Toward this goal, attempts were made to determine the position of the oxidation wave via cyclic voltammetry.

1) Results

The cyclic voltammograms (CV) for the potassium salts of the Si, B, and Zn polyoxotungstocuprate anions were recorded in three buffers: sulfate (pH = 2.2), acetate (pH = 4.7) and phosphate (pH =6.0). The concentrations were 5 x 10^{-3} M. Cyclic voltammograms were accomplished in both the positive potential region (0 to +2.0 V) and the negative potential region (0 to -2.0 V). The results for the negative sweeps are shown in Figures 6, 7, and 8 with the potentials tabulated in Table 2.

A 0.01 M acetate buffer solution of the potassium salt of $[SiW_{11}Cu(II)]^{6-}$ (0.79 g, 250 mmol) in 25 mL NaOAc/AcOH buffer (pH = 4.7) was electrolyzed at a controlled potential of -0.6 V. The extent of electrolysis was monitored by recording the decrease in size of the copper reduction CV wave at -0.45 V. At the completion of the eletrolysis, the CV showed this wave depleted and that 486 meq were used. The solution remained colorless throughout the electrolysis and a red-brown precipitate formed on the graphite cloth. No other precipitate was detected.

For the boron polyoxotungstocuprate, $[BW_{11}Cu(II)]^{7-}$, electrolysis was done at a potential just beyond the second wave at -0.48 V. The potassium salt of $[BW_{11}Cu(II)]^{7-}$ (0.82 g, 250 mmol) was dissolved in 25 mL of 0.1 M NaOAc buffer (pH = 4.7). Complete electrolysis was evidenced by the disapperance of both copper waves; a total of 494 meq was used. Again a red-brown precipitate

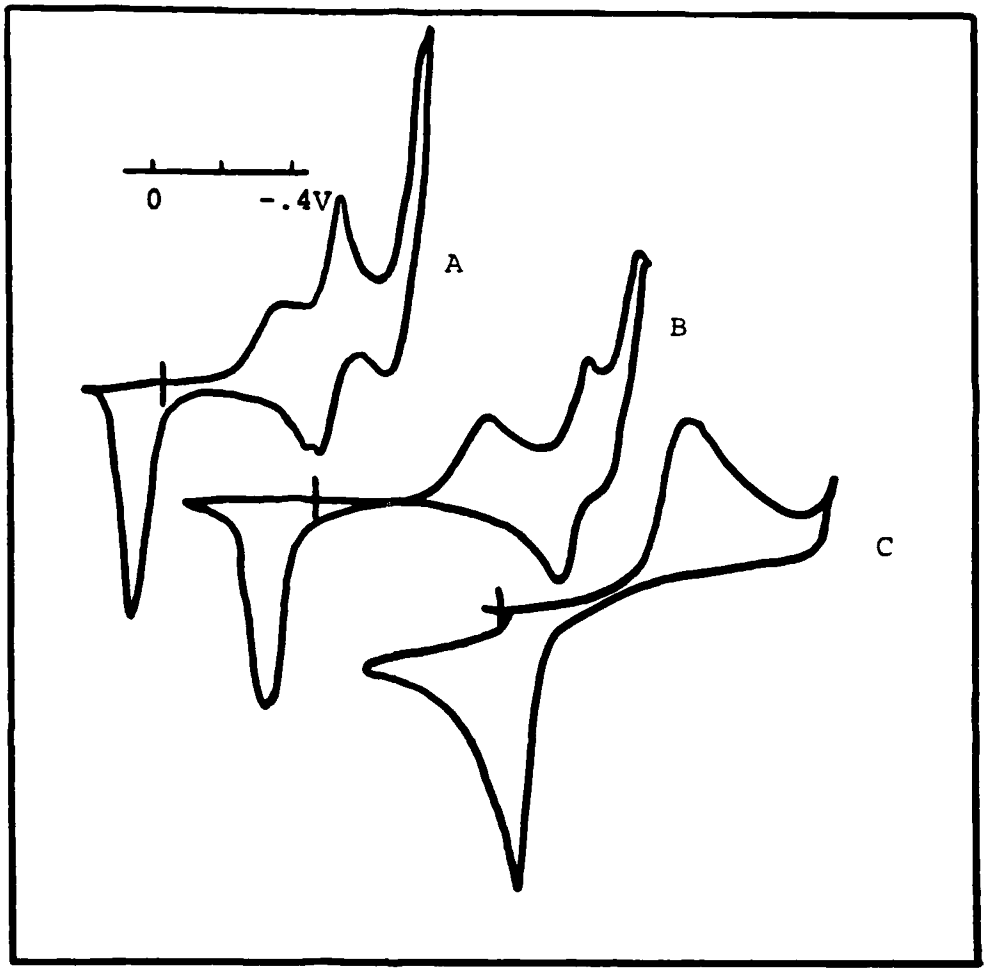

Figure 6: Cyclic voltammograms of .005 M $[SiW_{11}Cu(II)]^{6-}$ in (A) Sulfate Buffer (pH = 2.2), (B) Acetate Buffer (pH = 4.7), (C) Phosphate Buffer (pH = 6.0) as the K^+ salts. (Glassy carbon electrode vs. SCE; 2.0 V min^{-1})

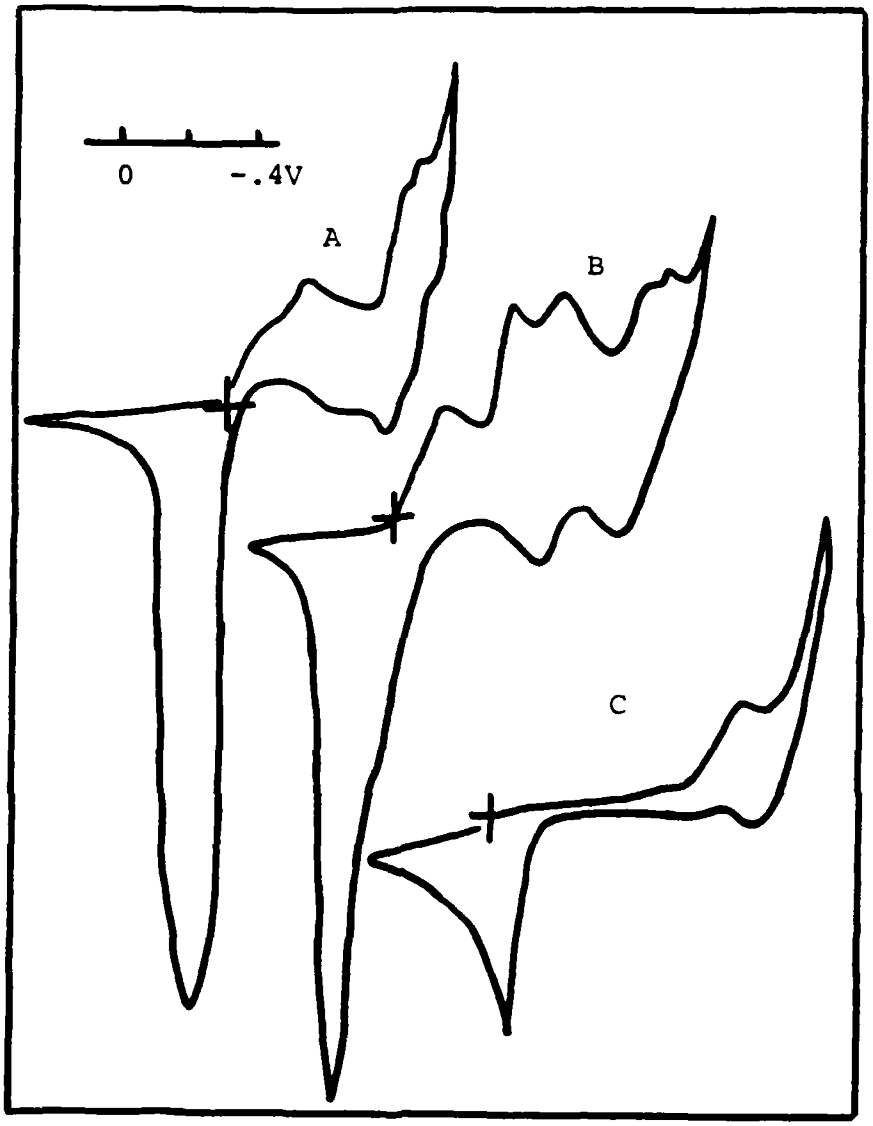

Figure 7: Cyclic voltammograms of .005 M $[BW_{11}Cu(II)]^{7-}$ in (A) Sulfate Buffer (pH = 2.2), (B) Acetate Buffer (pH = 4.7), (C) Phosphate Buffer (pH = 6.0) as the K^+ salts. (Glassy carbon electrode vs. SCE; 2.0 V min^{-1})

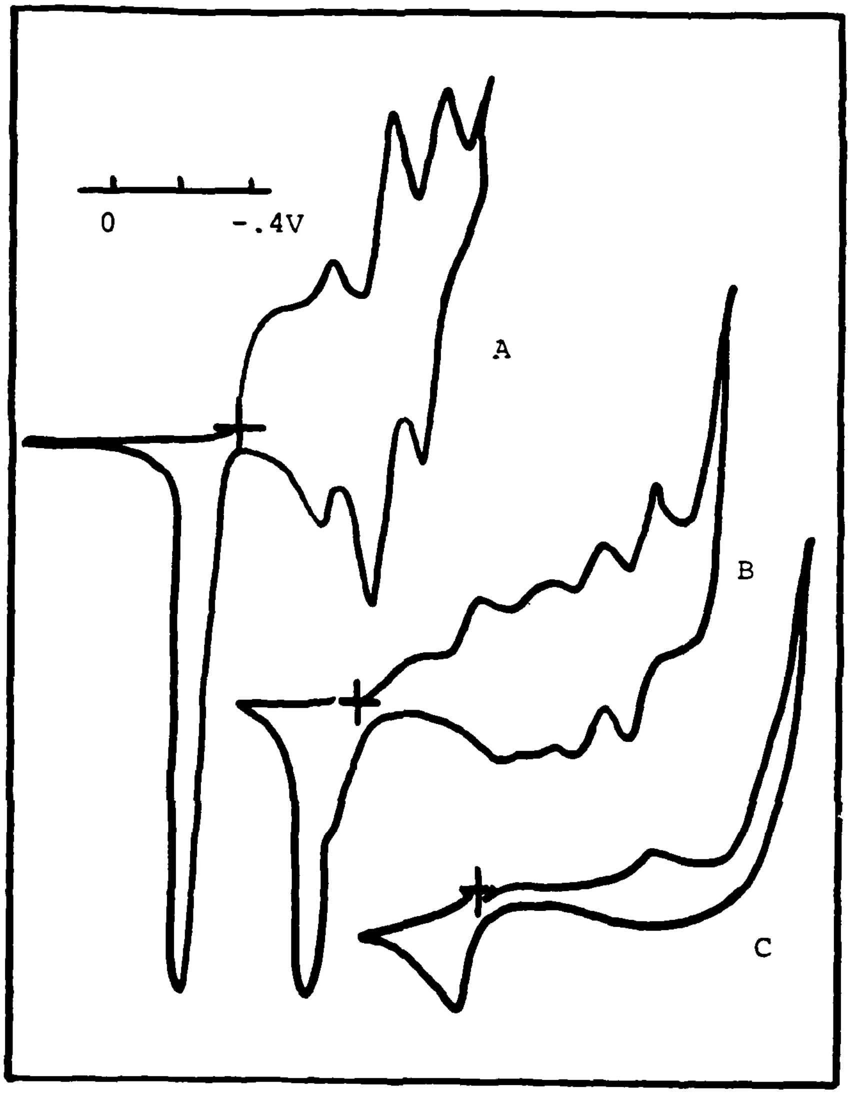

Figure 8: Cyclic Voltammograms of .005 M $[ZnW_{11}Cu(II)]^{8-}$ in (A) Sulfate Buffer (pH = 2.2), (B) Acetate Buffer (pH = 4.7), (C) Phosphate Buffer (pH = 6.0) as the K^+ salts. (Glassy carbon electrode vs. SCE; 2.0 V min^{-1})

TABLE 2

Voltammetric Data for Copper and Tungsten Reductions in $XW_{11}Cu(II)$ Anions in Various Buffers[a]

X	Sulfate pH = 2.2	Acetate pH = 4.7	Phosphate pH = 6.0
Si	-.34, -.49	-.48, -.75, -.89	-.53
B	-.23, -.5, -.55	-.14, -.32, -.45, -.68, -.76	-.4, -.73
Zn	-.1, -.25 -.42, -.55	-.15, -.33, -.54, -.67, -.82	-.46

[a] glassy carbon electrode vs. SCE; 2.0 V min^{-1}

formed on the graphite cloth.

2) Discussion

There was no evidence of copper oxidation in any of the three buffers as supported by the absence of an oxidation wave in the region 0 to +2.0 V. Thus in these heteropolyanions, the copper oxidation appears to be more positive than 1.8 V and in aqueous solution, Cu(III) could not be achieved.

In the negative potential region, both copper and tungsten redox processes are seen. The first reduction wave in each case appears to be the irreversible reduction of copper. This interpretation is supported by the fact that the reverse sweep yields the large reoxidation wave at +0.1 V. Subsequent reduction waves are typical reversible tungsten redox processes; placing the divalent copper atom in the lacunary position has very little effect on the reducibility of the polyanion.

In the acetate buffer solutions, sequential sweeps were done; that is, scans were made from the rest potential to each successive reduction wave and then the sweep reversed. Only for the Si polyoxotungstocuprate anion is there one reduction wave for copper. The B and Zn polyoxotungstocuprates show two copper reductions. Thus copper reduction occurs at -0.48 for $[SiW_{11}Cu(II)]^{6-}$ with reoxidation at +0.13 V. For $[BW_{11}Cu(II)]^{7-}$ reduction occurs at -0.14 and -0.32, while $[ZnW_{11}Cu(II)]^{8-}$ is reduced at -0.15 and -0.33. Both the boron and zinc complexes have a single copper reoxidation, at +0.15 and +0.12 respectively. In all three cases the reduction is not very reversible.

The two copper reductions for the B and Zn polyoxotungstocuprates may indicate the presence of two types of copper: copper in the heteropolyanion and free aquo copper(II). The cyclic voltammogram of a 5×10^{-3} solution of $Cu(NO_3)_2$ in 1.0 M NaAOc/HOAc buffer (46.8 mg, 20 mL buffer, pH = 4.7) shows two Cu(II) reduction waves at -0.1 V and -0.28 V; the reduction waves at -0.14 V and -0.15 V for B and Zn respectively match the first reduction wave for free aquo copper(II). Thus, there may have been free aquo Cu(II) and the Cu(II) in the heteropolyanion, each with a unique reduction potential but a common reoxidation. In the heteropolyanions where B and Zn form the central tetrahedron, copper may be less tightly bound and able to dissociate from the heteropolyanion.

The copper reduction is a two electron process as supported by the controlled potential electrolysis of both the Si and B polyoxotungstocuprate anions in acetate buffer. These results are in agreement with the findings for $[SiW_{11}Cu(II)]^{6-}$ reported by Teze[22]. He shows a two electron reduction process polarogram and states the reduction of Cu(II) complex yields Cu°. By analogy, the formation of the red-brown precipitate in the B polyoxotungstocuprate anion reduction indicates that $[BW_{11}Cu(II)]^{7-}$ also undergoes a two electron process.

When the potentials of both copper and tungsten redox proesses in the three buffers are compared, several trends emerge. First, the copper reduction shifts to more negative potentials as the pH of the solution increases. This suggests that copper remains in the heteropolyanion and its reduction potential depends on the solvent. For the boron heteropolyanion in acetate buffer and zinc in both sulfate and acetate buffer, the first reduction wave remains at essentially the same potential, -0.1 V, indicating this to be the free aquo copper(II). Considering the second wave to be the Cu(II) in the heteropolyanion, there is a shift of the copper reduction to more negative potentials in going from Si to B to Zn in any given buffer.

Second, the tungsten redox processes also shift to more negative potentials as the pH increases; in the phosphate buffer for Si and Zn the reduction is not seen suggesting the reduction potential has become more negative than -2.0 V.

B. Electron Spin Resonance

1) Results

The ESR spectra were obtained from 5×10^{-3} M solutions of the heteropolyanions in aqueous glycerol (1:1). Standard quartz cells were used and all spectra were obtained at liquid nitrogen (LN_2) temperatures. The resulting spectra for the K^+ salts of the three polyoxotungstocuprate anions are shown in Figure 9. Parameters for the coupling constant (A) and the center of gravity (g) values for the parallel hyperfines are listed in Table 3.

2) Discussion

The spectra are typical for d^9 Cu(II) atom with respect to both number of hyperfine lines and line broadening[23]. There are four hyperfine lines due to the coupling of the unpaired electron of Cu(II) with nuclear spin of 3/2 of both ^{63}Cu and ^{65}Cu. Sets of parallel and perpendicular hyperfine lines arise due to the distortion

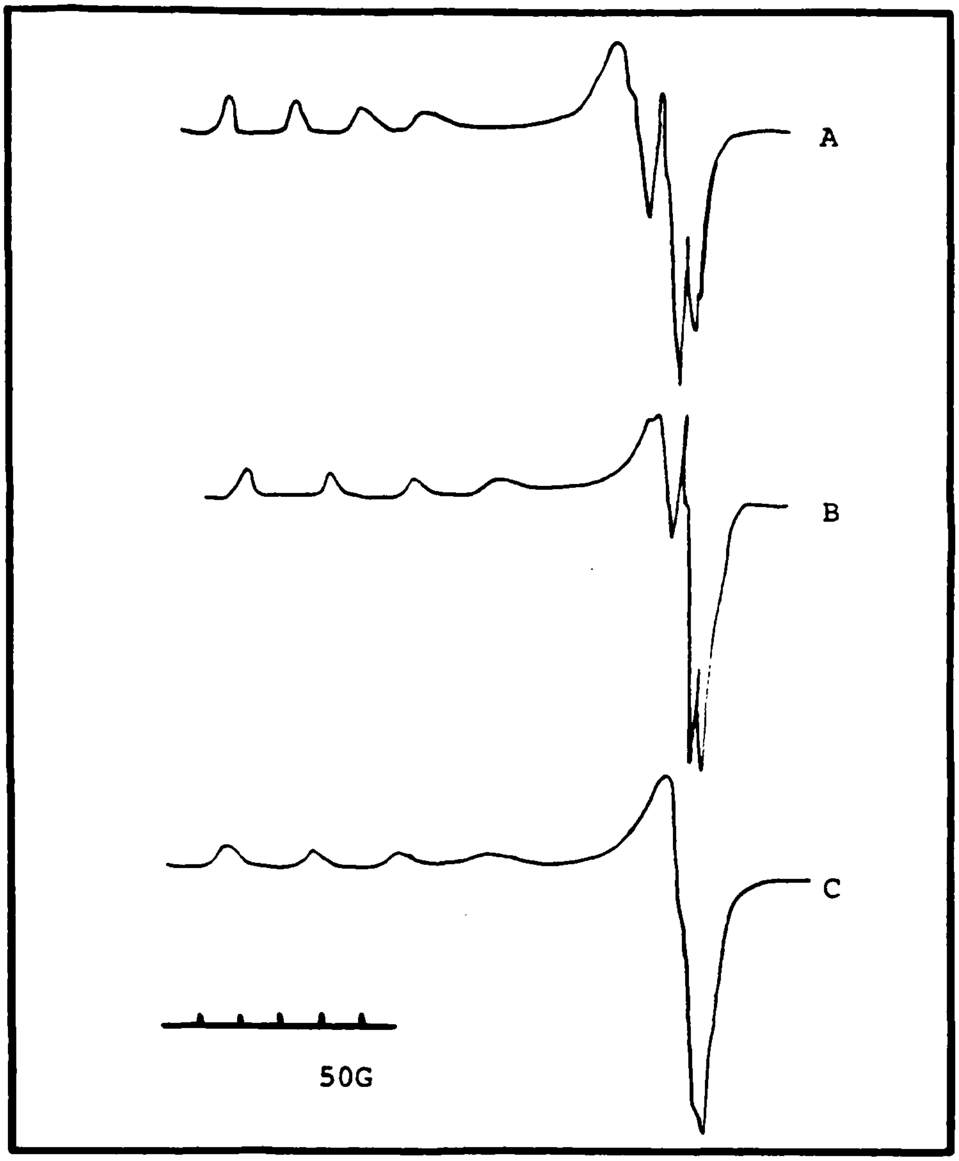

Figure 9: Electron spin resonance spectra of (A) $[SiW_{11}Cu(II)\text{-}OH_2]^{6-}$, (B) $[BW_{11}Cu(II)\text{-}OH_2]^{7-}$, and (C) $[ZnW_{11}Cu(II)\text{-}OH_2]^{8-}$ as K^+ salts in aqueous glycerol (c = 5 x 10^{-3} M; field set = 2900 G)

TABLE 3

ESR Parameters for K^+ Salts of $XW_{11}Cu(II)-OH_2$ in Aqueous Glycerol

5×10^{-3} M

X	$A_{\parallel}$	$g_{\parallel}$
Si	85.5G	2.43G
B	107.5G	2.39G
Zn	110.0G	2.41G

of the octahedra[24]. Line broadening is very typical of Cu(II) in aqueous solution. According to Fronisz[23], this broadening, which is especially pronounced when the ligands are oxygen atoms, results from the distribution of $A_{\parallel}$ and $g_{\parallel}$ values of the various populations of molecules present. These populations are made of differing strained Cu(II) heteropolyanions where strains have resulted from variations in the in-plane π-bonding accompained by smaller but still significant changes in the in-plane σ-bonding, Each Cu(II) is thus in a slightly different environment and each molecule has its own ESR spectrum with individual A and g values. The final ESR spectrum represents the sum of these individual spectra[23]. At low field, the $A_{\parallel}$ and $g_{\parallel}$ values are more nearly identical for the entire populaion but at higher field the values differ more widely and broadening results.

The $A_{\parallel}$ values reported in Table 3 are in the range of 120 G, typical of the previously reported ligand-on value; in aqueous solution, $-OH_2$ is the fifth ligand. However, there is an inverse relationship between the anion charge and the $A_{\parallel}$ value as depicted in Figure 10. As the charge on the heteropolyanion becomes more negative (as the central tetrahedral heteroatom becomes less positive) the

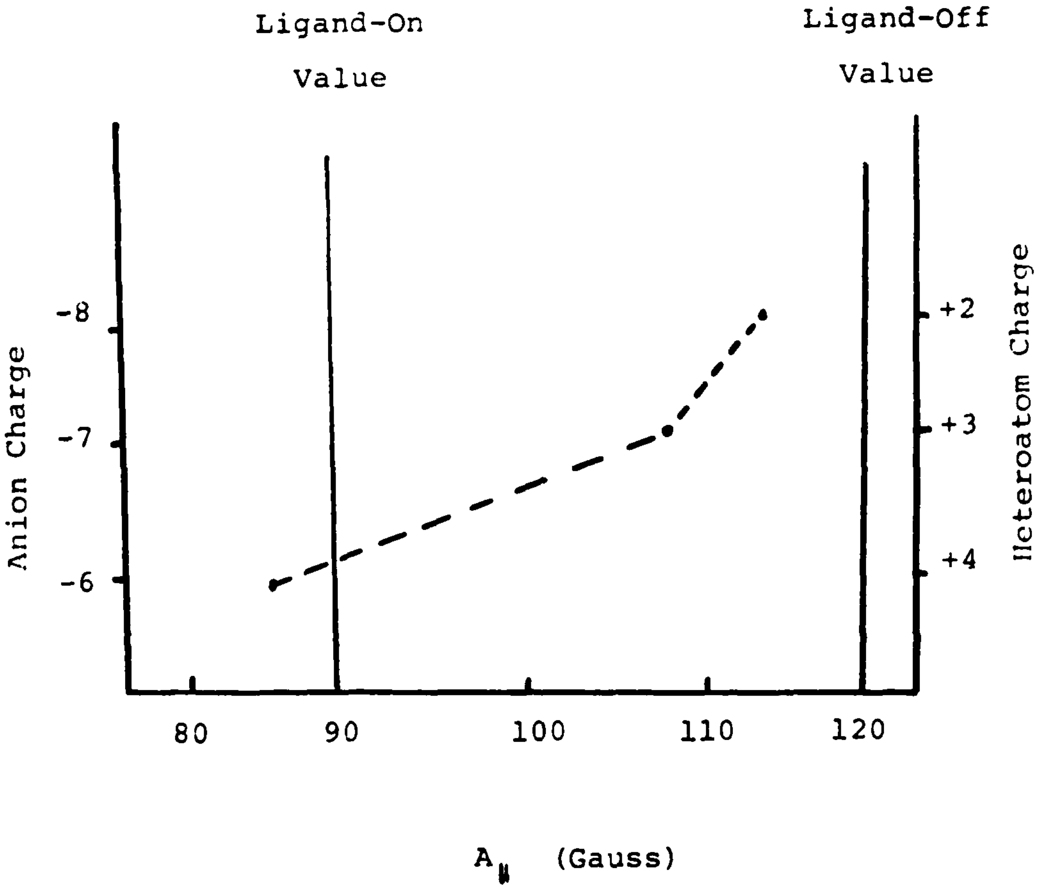

Figure 10: Inverse relationship of anion charge and $A_{\parallel}$ value for $XW_{11}Cu(II)-OH_2$ complexes

$A_\parallel$ value increases and approaches that of the ligand-off value. This suggests that the boron and zinc heteropolyanions solutions have both ligand-on and ligand-off species present. The apparent loss of the water ligand is supported by the near-IR absorption spectra. Recalling Katsoulis' work[7], the ligand-on spectrum has a lower energy absorbance (λ = 880 nm) than the ligand-off spectrum (λ = 710 nm). The near-IR spectra of these heteropolyanions (Fig 4) shows a shift to higher energy absorbances in going from Si to B to Zn (875 nm to 765 nm to 790 nm) - a shift toward values typical of the ligand-off condition. Thus both spectroscopic measurements indicate that in both boron and zinc heteropolyanions, two copper species, hydrated and non-hydrated, may be present.

Attempts were made at computer simulation of the spectra using PROGRAM CURHEPR. Resulting spectra did not accurately simulate the line broadening in either the parallel or perpendicular regions. In the parallel region, the computer linewidths were too small while in the perpendicular region they were too large. Variations of all the input parameters failed to adjust the relative spacing between the lines; their field position could be shifted but the spacings remained constant. Thus, apparent A and g values are reported throughout.

3. Non-Aqueous Chemistry

A. Electronic Absorption Spectra: Near-Infrared Region

1) Results

Near-IR absorbances for both the protonated and deprotonated $[SiW_{11}Cu(II)]^{6-}$ anions were recorded at concentrations of 0.01 M in 1 cm cells; the spectra are shown in Figure 11 and absorbance maxima are in Table 4.

2) Discussion

In this region, the absorbance is due to the d-d electron transitions in copper. The absorption bands for the deprotonated species, $[SiW_{11}Cu(II)]^{6-}$ in both "wet" and "dry" toluene and CH_3CN are typical of the ligand-off value of 720 nm[7]. On the other hand, the absorption band of the protonated complex, $[H_2SiW_{11}Cu(II)]^{4-}$ occurs at 800 nm. The shift is attributed to protonation rather than the binding of a water molecule (recall that the aquoanion has $\lambda_{max} = 875$). It seems likely that the oxygen atoms adjacent to Cu(II) are the most basic in this structure. Titration showed the presence of two protons and these could be bound to any of the four oxygens giving rise to four diastereomers. The ESR spectum (Chapter III, Section 3) shows two sets of

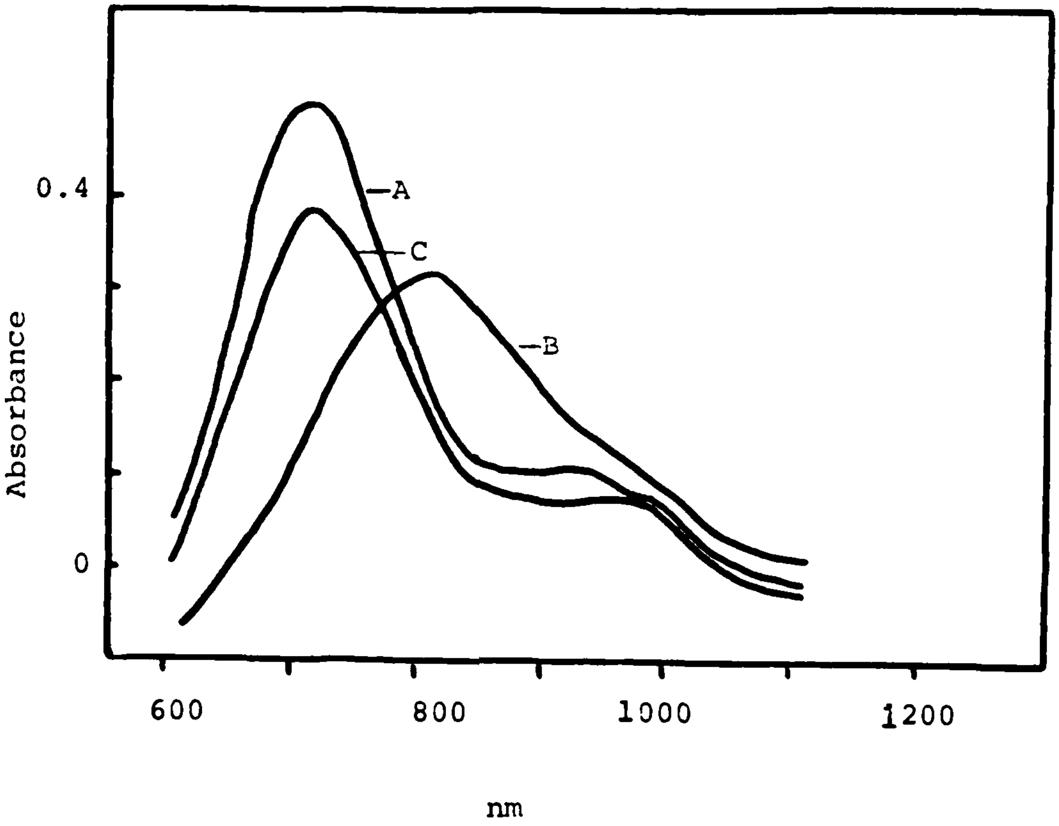

Figure 11: Near-infrared absorption spectra of (A) $[SiW_{11}Cu(II)]^{6-}$ as THpAB salt in toluene; (B) $[H_2SiW_{11}Cu(II)\text{-}OH_2]^{4-}$, and (C) $[SiW_{11}Cu(II)]^{6-}$ as TBA salts in CH_3CN (c = 0.01 M; path length = 1 cm)

TABLE 4

Electronic Absorption Maxima of Cu(II) in Protonated and Deprotonated SiW_{11} Anions in Organic Solvents

Near-IR Region

$c = 1 \times 10^{-2}$ M

Anion	Band (nm)	ε (M^{-1} cm^{-1})
$[SiW_{11}Cu(II)]^{6-}$ in		
dry toluene[a]	720	30
wet toluene[b]	723	
$[H_2SiW_{11}Cu(II)]^{4-}$ in		
wet CH_3CN[c]	800	16
$[SiW_{11}Cu(II)]^{6-}$ in		
dry CH_3CN[a]	717	19.6
wet CH_3CN[c]		

[a] as described in Chapter III, Section C.

[b] after extraction, solvent not dried

[c] solvent not dried

hyperfine lines which might result from two such isomers.

B. Electrochemistry

1) Results

Cyclic voltammograms (CV) of both $[H_2SiW_{11}Cu(II)]^{4-}$ and $[SiW_{11}Cu(II)]^{6-}$ were recorded for 5 x 10^{-3} M solutions in CH_3CN with 5 x 10^{-2} M $TBAClO_4$ (in CH_3CN) as the supporting electrolyte. The voltammograms were obtained with a glassy carbon electrode vs SCE at a sweep rate of 2.0 V min^{-1}. Both the positive (0 to +2.0 V) and negative (0 to -2.0 V) regions were scanned. The CVs are shown in Figure 12 and the potential data in Table 5.

Controlled potential electrolysis was done on the deprotonated $[SiW_{11}Cu(II)]^{6-}$ anion. From the previously dried solution of $SiW_{11}Cu(II)$ in CH_3CN, 13 mL of a 3.25 x 10^{-3} solution (84.5 mmol) in 0.1 M $TBAClO_4/CH_3CN$ was electrolyzed just past the first reduction wave at -1.0 V. The electrolysis was monitored via cyclic voltammetry and determined complete at the disappearance of the reduction wave at -1.0 V. A total of 195 meq were required for completion (ratio of meq/mmol = 2.3). The solution turned from the initial aqua color to brown-yellow. The electrolysis was continued to 286 meq (ratio = 3.4). The

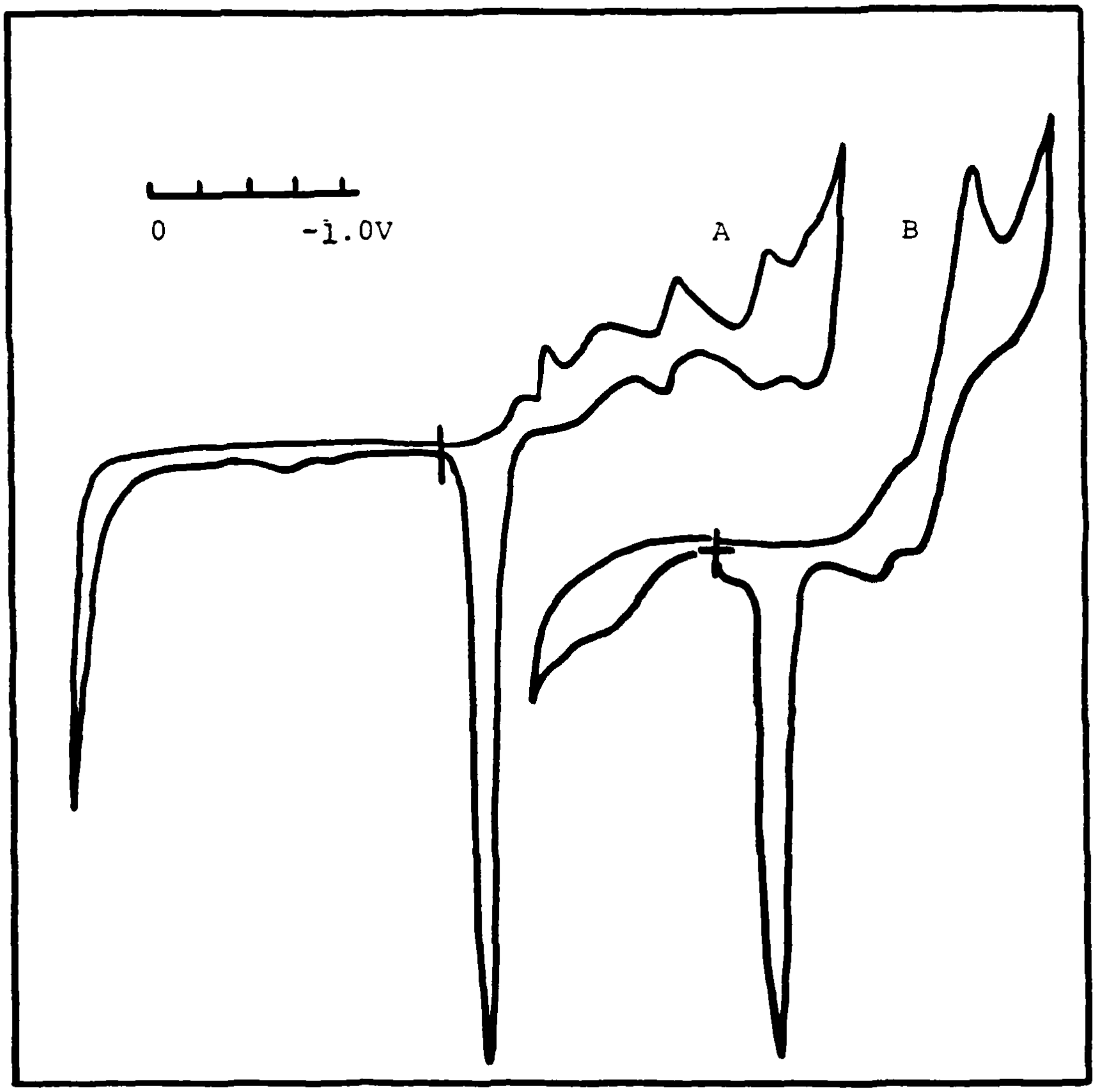

Figure 12: Cyclic voltammograms of (A) $[H_2SiW_{11}Cu(II)\text{-}OH_2]^{4-}$ and (B) $[SiW_{11}Cu(II)]^{6-}$ as TBA salts in CH_3CN (glassy carbon electrode vs. SCE; sweep = 2.0 V min^{-1})

TABLE 5

Voltammetric Data for Tungsten Redox Processes of $SiW_{11}Cu(II)$ as TBA Salts in Acetonitrile [a]

	Reduction	Oxidation
$[H_2SiW_{11}Cu(II)\text{-}OH_2]^{4-}$	-.43, -.5, -.9 -1.3, -1.7	+.83, -.18, -.65 -1.2, -1.7
$[SiW_{11}Cu(II)]^{6-}$	-.9, -1.4	+.56, -.33 -.85, -1.1

[a] glassy carbon electrode vs SCE; 2.0 V min^{-}

solution turned dark green but returned to brown upon exposure to atmospheric oxygen. No red-brown precipitate was observed on the graphite cloth as with the silicon and boron heteropolyanions in aqueous solution.

2) Discussion

In scanning the positive potential region, a small oxidation wave at +0.56 V was seen in the $[SiW_{11}Cu(II)]^{6-}/CH_3CN$ solution. However, this wave does not appear to be copper oxidation since various attempts to oxidize the copper were unsuccessful.

Considering the negative region of the CV, the complex cyclic voltammogram for the protonated heteropolyanion, $[H_2SiW_{11}Cu(II)\text{-}OH_2]^{4-}$ indicates a complex reduction process. Doing a sequential sweep as described for the aqueous experiment, the CV shows the first two reduction waves have a single reoxidation wave. That is, upon sweeping successively to -0.43 and -0.55, the only reoxidation wave seen on the return sweep is at -0.18. The intensity of the wave increases after sweeping to the second reduction wave indicating the generation of yet more copper. Thus again there appear to be two copper(II) species present. There may be copper in or out of the heteropoly as described for the aqueous heteropolyanions or there may be singly or doubly protonated anion present with Cu(II) in the heteropolyanion. The copper processes are not very reversible in contrast to the tungsten redox process.

The deprotonated heteropolyanion, $[SiW_{11}Cu(II)]^{6-}$, under the same concentration and solvent conditions, shows a much simplier CV (Fig 13). Identification of the redox processes was accomplished as above and the results are listed in Table 5. Here, a single copper reduction indicates one reducible copper species. The main difference in organic solvents as compared to the aqueous solution, is the shift to more negative potentials for both copper and tungsten reductions. The shift is ca. -0.4 V for copper and ca. -0.6 V for tungsten. In going to the dry organic solution of the deprotonated heteropolyanion, where $-OH_2$ ligand has been removed from the copper, the reductions of both copper and tungsten become more negative. This is also true for the protonated heteropolyanion although the shift is not so great.

The solution resulting from the controlled potential electrolysis of the deprotonated $[SiW_{11}Cu(II)]^{6-}$ anion in CH_3CN was brown as described above. To account for the brown color of the solution, it was thought that despite the addition of two electrons, perhaps Cu(I) had indeed formed, giving rise to the brown color indicative of many Cu(I) complexes[15.b]. Thus if Cu(I) were present, reoxidation should restore Cu(II) and the aqua color. Electrolysis was carried out at +1.0 V but the brown color remained. Near-IR spectra of the solution after electrical reduction and after reoxidation, show the absence of Cu(II) absorbance in the expected 700 nm region. The electrolysis does show a two electron reduction process in organic solvents as well as in the aqueous solutions.

C. Electron Spin Resonance

1) Results

ESR spectra of both the protonated and deprotonated $SiW_{11}Cu(II)$ anions are shown in Figure 13. Concentrations were approximately 0.01 M and spectra were obtained at 77 K (LN_2). Parallel hyperfine values are reported in Table 6.

2) Discussion

The ESR spectra of the dry toluene and CH_3CN solutions show only one species present and the $A_{\parallel}$ value of 120 G is typical of the ligand-off condition. This finding correlates well with the near-IR absorbance value of 720 nm. To confirm the binding of the water molecule,

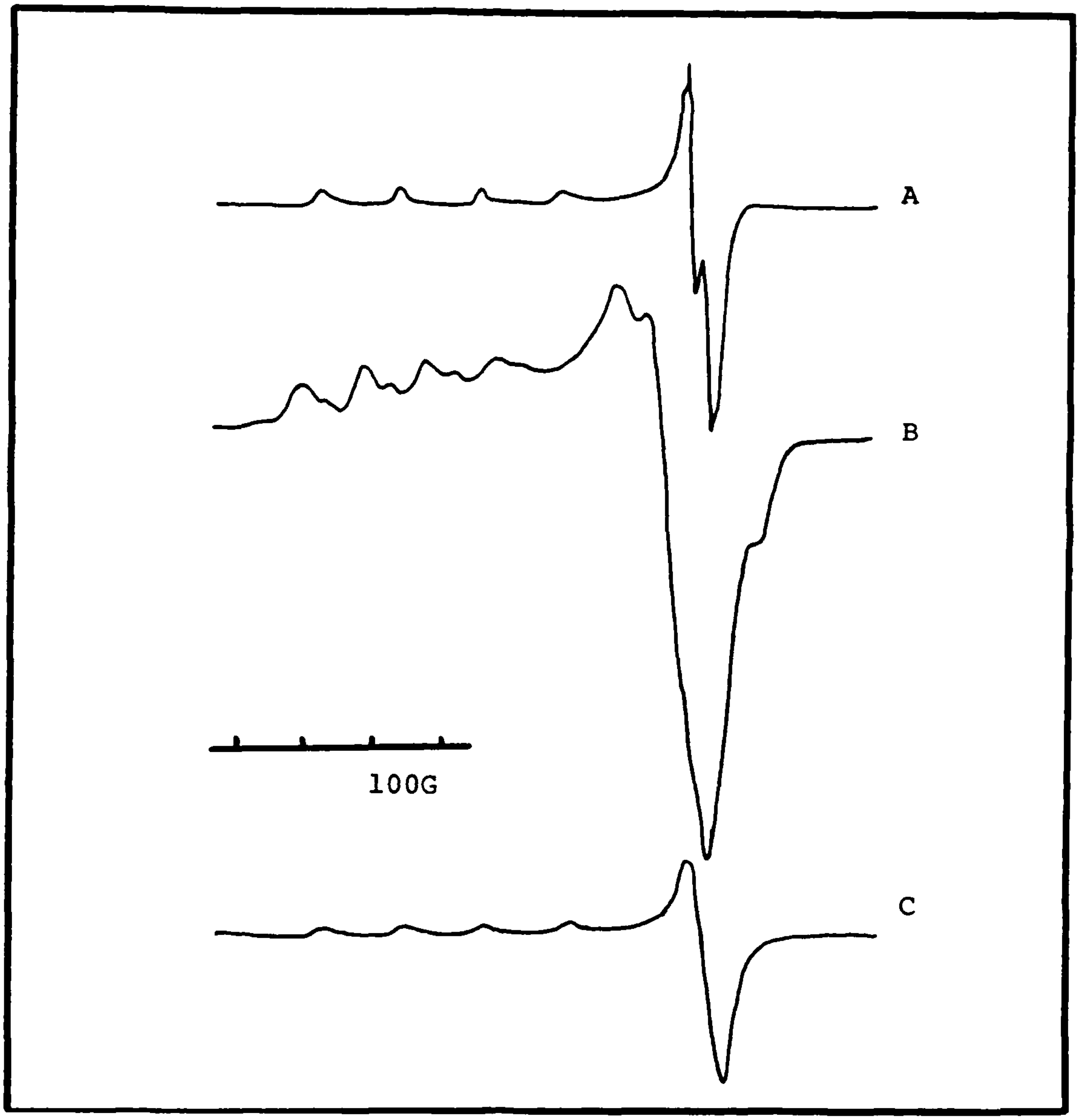

Figure 13: Electron spin resonance spectra of (A) $[SiW_{11}Cu(II)]^{6-}$ as THpAB salt in toluene; (B) $[H_2SiW_{11}Cu(II)\text{-}OH_2]^{4-}$ and (C) $[SiW_{11}Cu(II)]^{6-}$ as TBA salts in CH_3CN. ($c = 5 \times 10^{-3}$ M; field set = 2900 G)

TABLE 6

ESR Parameters for $[SiW_{11}Cu(II)]$ Anions in Organic Solvents

Anion	$A_\parallel$	$g_\parallel$
$[SiW_{11}Cu(II)]^{6-}$/toluene	120G	2.36G
$[SiW_{11}Cu(II)]^{6-}$/CH_3CN	121G	2.34G
$[H_2SiW_{11}Cu(II)\text{-}OH_2]^{4-}$/$CH_3CN$	97G	2.42G
	98.5G	2.39G

the dry CH_3CN heteropolyanion solution was mixed with water in a 1:1 volume ratio. The ESR showed only one set of hyperfine lines with an $A_{\parallel}$ value of 90 G - the ligand-on value. Thus the ligand-on structure can be restored in organic solvents.

The ESR spectrum of the protonated complex shows the presence of two species with $A_{\parallel}$ values of 97.0 and 98.7 G and $g_{\parallel}$ values of 2.42 and 2.39 respectively. As with the near-IR absorbance values, these ESR values lie intermediate to the ligand-on and ligand-off values. The results are attributed to the protonated species rather than the binding of a water molecule. The two species seen in the ESR spectrum may result from isomers arising from the four probable protonation sites around copper(II). Four diastereomers are possible for the diprotonated anion. Addition of protons to the deprotonated heteropolyanion was conducted to restore the protonated species. Addition of 3.75 mL of 0.017 M triflic acid (CF_3SO_3H, Aldrich Chemical; 0.15 mL of 11.3 M acid diluted to 100 mL with CH_3CN; 0.064 moles), to 2 mL of 8.55 x 10^{-3} M (0.017 moles) $[SiW_{11}Cu(II)]^{6-}$ in CH_3CN did not produce a colorless solution. However, addition of 2 drops (0.1 mL) of the undiluted 11.3 M triflic acid caused the solution to turn colorless (total moles H^+ added = 1.2×10^{-3}; ratio H^+:HPA = 14:1). The ESR spectrum of this reprotonated solution showed a single set of hyperfine lines with $A_{\parallel}$ equal to 100 G and $g_{\parallel} = 2.43$. The loss of the two sets of hyperfine lines was attributed to the excess protons added; possibly all four oxygen atoms had become protonated.

As with the aqueous heteropolyanions, computer simulations of the ESR spectra were attempted without success. Again, the lack of input parameters for the line broadening known to occur for copper(II) prevented the accurate simulation of the experimental spectra. Linewidths in both the parallel and perpendiuclar regions were inaccurately reproduced. Reported $A_{\parallel}$ and $g_{\perp}$ values are therefore apparent values, uncorrected for second-order effects.

D. Reaction with O_2

While the oxidation potential of copper is much greater than that of O_2, reaction with molecular oxygen was not expected to produce Cu(III). However, the reaction was carried out to determine if O_2 would bind to copper(II) as a fifth ligand.

1) Results

Initially atmospheric oxidation was attempted. Twenty-five mL of a 0.01M solution of the potassium salt of $SiW_{11}Cu(II)$ in toluene was placed in a closed vial. Under these conditions, Mn was oxidized[7] but Cu(II) was not. The solution color did not change after one week. Next, O_2 was bubbled, at room temperature, through a 3 mm test tube filled with 25 mL of the solution; the O_2 first passed through a dried toluene bubbler to prevent loss of solvent. The color of the solution did not change after two hours of bubbling; the near-IR spectrum was identical to that of the starting material (Fig 11); the maximum absorbance still occured at 717 nm. The ESR spectrum of this solution was also unchanged from that of the starting material (Fig 13). The experiment was carried out at low temperature by placing the test tube containing the solution just exposed to O_2 for two hours, into a Dewar containing dry ice and acetone (0° C). Again, O_2 was bubbled through the solution with no change in color; a blanket of O_2 was left over the solution for two days with still no change in color. The absorption and ESR spectra showed no change from those obtained after the room temperture treatment.

The experiment was repeated for $[SiW_{11}Cu(II)]^{6-}$ in dry acetonitrile. At room temperature, no color change from aqua was observed; the ESR spetrum of the solution was again identical to the original (Fig 13). The low temperature experiment was carried out under the conditions described above. No color change was detected and the ESR spectrum showed no significant change from that obtained after the room temperature treatment.

2) Discussion

It appears that O_2 does not bind strongly enough to Cu(II) while in the tungstosilicato anion to appreciabley alter the spectroscopic properties. The possibility can not be ruled out that O_2 does not form a weak complex with Cu(II); but, if it does, the proportion of oxygenated product is insufficient to observe by the spectroscopic techniques employed.

E. Reaction with Br_2

Bromine has a high reduction potential (+1.07, in acid solution)[5.b] and is commonly used as an oxidizing agent. The cyclic voltammogram (Fig 12) of $[SiW_{11}Cu(II)]^{6-}$ in CH_3CN showed a very small oxidation wave at +0.56; if this wave were indeed the oxidation of Cu (II), Br_2 should be able to oxidize the copper from a thermodynamic standpoint. However, oxidation may still not be possible as other factors may preclude the Br_2 from forming the adduct with copper (II) necessary for the inner-sphere electron transfer.

1) Results

The experiment was conducted with benzene as the solvent for both Br_2 and $[SiW_{11}Cu(II)]^{6-}$. A red Br_2/benzene solution was prepared (5 drops Br_2, d = 3.119, in 10 mL benzene; concentration = ca. 0.5 M). Twenty-five mL of a 0.01 M solution of the THpAB salt of $[SiW_{11}CuII]^{6-}$ (as prepared in Chaper III, Section C) was dried by bubbling N_2 through the solution for 2 hours. Five mL of each solution were then mixed at room temperature (5×10^{-5} moles $[SiW_{11}CuII]^{6-}$ plus 2.4×10^{-3} moles Br_2). The color of the solution turned from aqua to pale yellow green. Despite the color change, the near-infrared spectra of this solution was identical to that of the starting material (Fig 11), with λ_{max} = 717 nm. The reacted solution was warmed to ca. 50° C with stirring for ca. 5 minutes; no further change in solution color resulted.

2) Discussion

Br_2 does not oxidize Cu(II) in the tungstosilicato anion as it does Mn(II). Despite the change in solution color, Cu(II) was not oxidized as evidenced by the strong absorbance at 717 nm characteristic of copper(II) identical to the starting matrial. Some Cu(III) complexes have absorbances at 295 - 310 nm[13.d] and a scan in this region did show absorbance (Line C, Fig 14). But heteropolyanion/benzene and Br_2/benzene starting materials (Lines A and B, Fig 14) also absorb here; the spectrum of the reacted solution is identical to the unreacted solution. However, the absorbance at 414 nm in the Br_2/benzene starting material disappears after reaction. This absorbance also disappears when Br_2/benzene is reacted with a blank solution containing only THpABr in benzene, the other species in the heteropoly solution. The Br_2/benzene solution is changed as evidenced by the disappearance of the absorption at

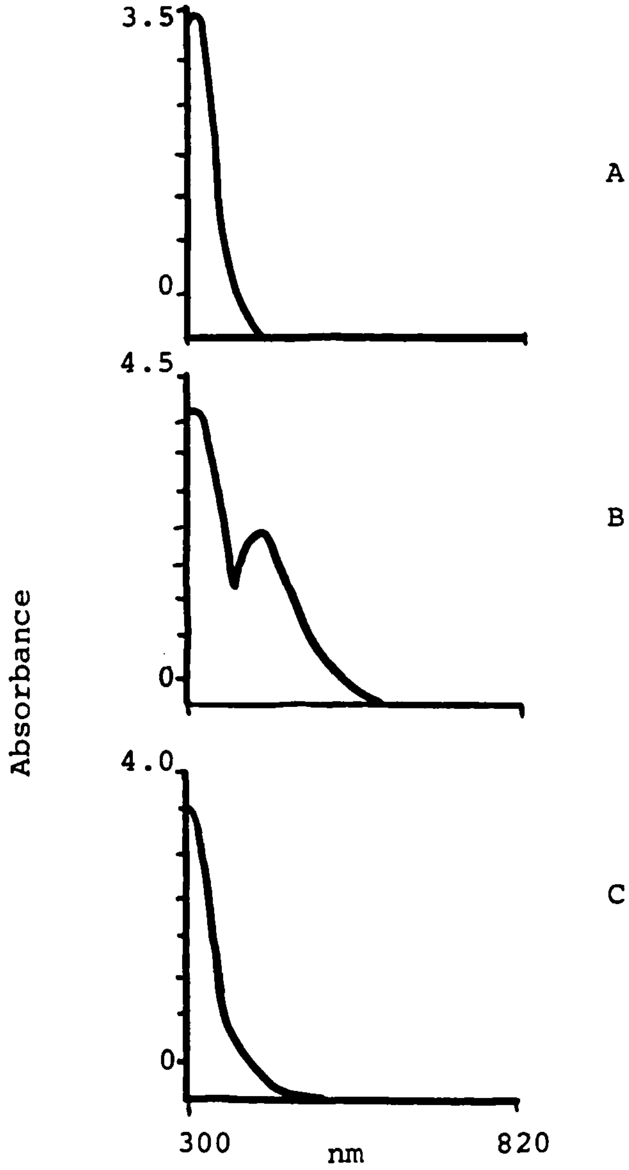

Figure 14: Ultra-violet absorption spectra of (A) 0.01 M $[SiW_{11}Cu(II)]^{6-}$ as the THpAB salt in benzene, (B) ca. 0.5 M Br_2/benzene and (C) (C) $[SiW_{11}Cu(II)]^{6-}$ + Br_2 in Benzene after reaction (path length = 1 cm).

414 nm and by the color change in the solution. Since Br_2 does not react with the heteropoly itself, it is possible that Br_2 reacts with the quarternary ammonium salt. Several possibilities exist: 1) a subsitution reaction where the alkyl side chain is brominated (forming the brominated quarternary salt or an amine and a brominated alkyl group[25]); 2) an elimination reaction where the unsaturated alkene side group is formed[25]; or 3) formation of Br_3^- by reaction with Br^- carried into benzene during the extraction and Br_3^- ion pairs with $THpA^+$ [26]. If bromination of the alkyl group occurs or if an elimination reaction takes place, ^1H NMR of the reacted material would differ from the starting material. In both cases, proton peak intensity at the reacted site would decrease and if bromination occurs, a downfield chemical shift would be seen. The NMR spectra of the two solutions were identical except for a small upfield chemical shift of the α-CH_2. According to Dr. Hammer[26], structural change has not occurred but Br_3^- is indicated. The α-CH_2 group would shift upfield if a new anion formed the ion pair; changing Br^- for Br_3^- could cause this shift. The critical fact is that bromination of the alkyl chain does not appear to occur and the use of Br_2 to oxidize metals

in the heteropolyanion is effective.

Thus, the oxidation wave at +0.56 V is not likely to be that of Cu(II) ----> Cu(III) since Br_2, whose potential is more than sufficient to oxidize it, does not. However, since this reaction would probably proceed via an inner-sphere electron transfer mechanism [7], a ligand on the copper would prevent the formation of the copper-Br_2 adduct, making oxidation impossible. Initially, the reaction was attemped with CH_3CN as the solvent. This too was unsuccessful. Spectroscopic measures indicated that CH_3CN does not form a fifth ligand on copper as discussed in Chapter III, Section 3.A. The near-IR absorbance at 717 nm is indicative of the ligand-off complex and ESR spectra showed the presence of only one species with an $A_\parallel$ value typical of the ligand-off complex. However, as a check, the experiment was repeated in benzene as described above since it is known that benzene does not form a fifth ligand and leaves the copper open for reaction[7]. The reaction results were the same. From these results it appears the oxidation of Cu(II) in the heteropolyanion is not +0.56 V and that it is greater than +1.07 V. Also the spectroscopic evidence support that neither CH_3CN nor benzene form the fifth ligand on the copper.

F. Reaction with Superoxide Anion (O_2^-)

Potassium superoxide (KO_2) has been recognized as a source of the O_2^- anion since 1934 [27.a], and recent studies have focused on the superoxide dismutase enzyme[28.a]. These metalloenzymes are postulated to play a protective role in cells by reducing levels of O_2^- [28.a], which accumulates in the cells during aerobic mechanisms and must be removed. The metalloenzymes contain either copper and zinc or iron and manganese[15.a] and the metal is critical in the catalysis of O_2^- dismutation. The following scheme is proposed by Valentine[15.b]:

$$\text{Enz-Cu(II)} + O_2^- \dashrightarrow \text{Enz-Cu(I)} + O_2$$

$$\text{Enz-Cu(I)} + 2\,H^+ + O_2^- \dashrightarrow \text{Enz-Cu(II)} + H_2O_2$$

$$\text{Overall: } 2\,O_2^- + 2\,H^+ \dashrightarrow O_2 + H_2O_2$$

Scheme I

Valentine studied $[Cu(phen)_2]ClO_4)_2$ in DMSO and found[15.b] that reaction with KO_2 solutions gave deep brown solutions of the Cu(I) complex, $[Cu(phen)_2]ClO_4$.

The chemistry of the superoxide ion is characterized by its strong nucleophilicity[27.b] and in aprotic media it is an effective reducing agent for copper(II)[27.c]. The redox potentials for O_2/O_2^- (vs SCE) in CH_3CN and DMSO are -0.78 and -0.75V respectively[28.b]. The copper(II) reduction potential in the tungstosilico anion in CH_3CN (Fig 12) is more negative than this and O_2^- would not be expected to reduce Cu(II). However, reaction with Cu(II) and O_2^- was investigated to see if O_2^- would bind to the metal.

1) Results

a) Preparation of O_2^- Solution

There are several preparative methods for organic solutions of O_2^-: 1) electrochemical - the controlled reduction of dioxygen[28.c]; 2) solubilization of KO_2 using crown ethers [28.b]; and 3) direct solubilization of KO_2[29]. Of these three methods, direct solubilization was selected as the most convenient. While Valentine reports the need for crown ethers to prepare relatively concentrated solutions in DMSO (solutions of O_2^- in CH_3CN or dimethylformamide are relatively unstable)[28.b], Harbour reports good results in DMSO without the use of phase transfer agents. In fact, in the presence 18-crown-6-ether the ESR spectrum of O_2^- in DMSO was broadened as compared to that without the crown ether[29].

Thus, O_2^-/DMSO solutions were prepared as follows.

Preparation of O_2^- solutions and O_2^- reactions with the heteropolyanion were conducted in the dry box (Vacuum Atmosphere Company) to avoid disproportionation of O_2^- by H_2O or H^+ ($2O_2^- + 2\ H^+ \longrightarrow O_2 + H_2O_2$)[28.a]. Potassium superoxide (KO_2, Fluka AG) was finely ground and 710 mg (1.0 mmole) was added to 20 mL dry DMSO. The solution was stirred for 1.5 hours. Not all the solid material disolved. The visible spectrum of the golden-yellow supernatant liquid was taken and compared with published data [28.d]. Results are in Figure 15. Using the published ε value of 2686±29 and the absorbance at $\lambda_{max} = 258$ nm, the concentration was calculated to be 8.7×10^{-3} M. The stability of this solution over time was monitored. Although the maximum absorbance remains at 258 nm, a new peak at 330 nm appears after 24 hours and increases in size with time (Fig 16). This peak was presumed due to decomposition and thus to ensure a stable O_2^- solution, the O_2^-/DMSO solutions were prepared just prior to all reactions. Concentrations and product purity were taken from visible spectra each time and reaction stoichiometry calculated from this. The ESR specrum of the O_2^- solution (Figure 17) shows a very broad line.

b) Reaction of O_2^- with $[SiW_{11}Cu(II)]^{6-}$ in Toluene

O_2^-/DMSO solutions were reacted with

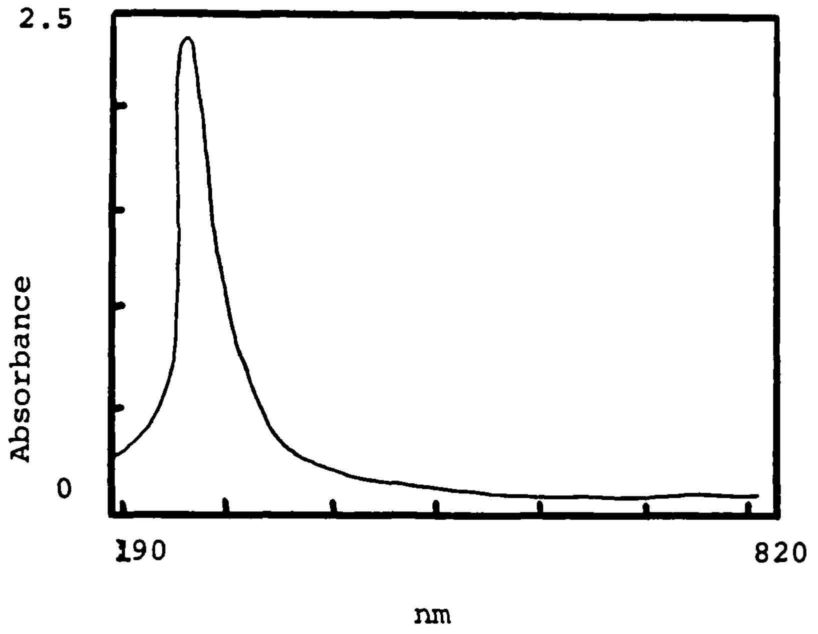

Figure 15: Visible spectrum of ca. 8.7 x 10^{-3} M KO_2 in DMSO (ε = 2686 ± 29, λ_{max} = 258, path length = 1 cm, reference = DMSO)

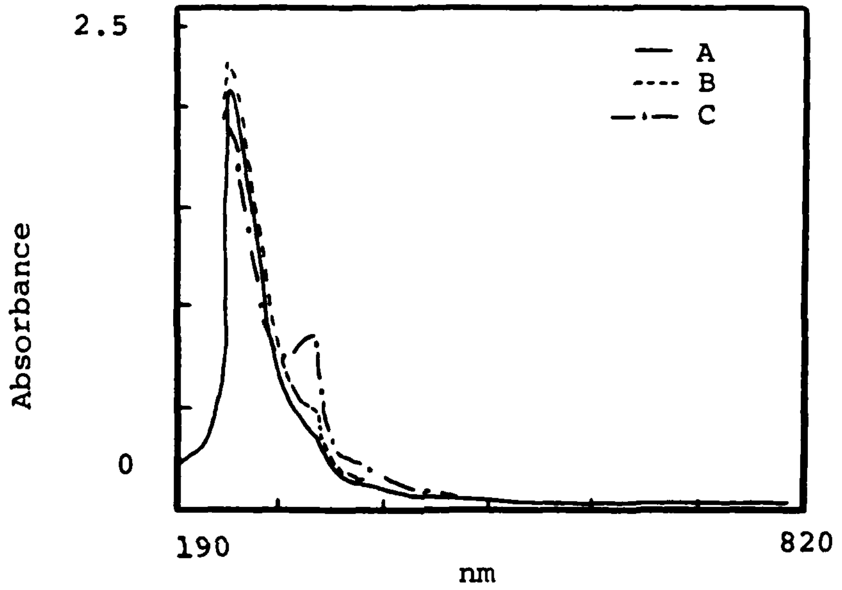

Figure 16: Visible spectra of KO_2/DMSO over time; appearance of absorbance at λ_{max} = 331 (A) 24 hours (B) 48 hours (C) 14 days (c = ca. 8 x 10^{-3}, path length = 1 cm, reference = DMSO)

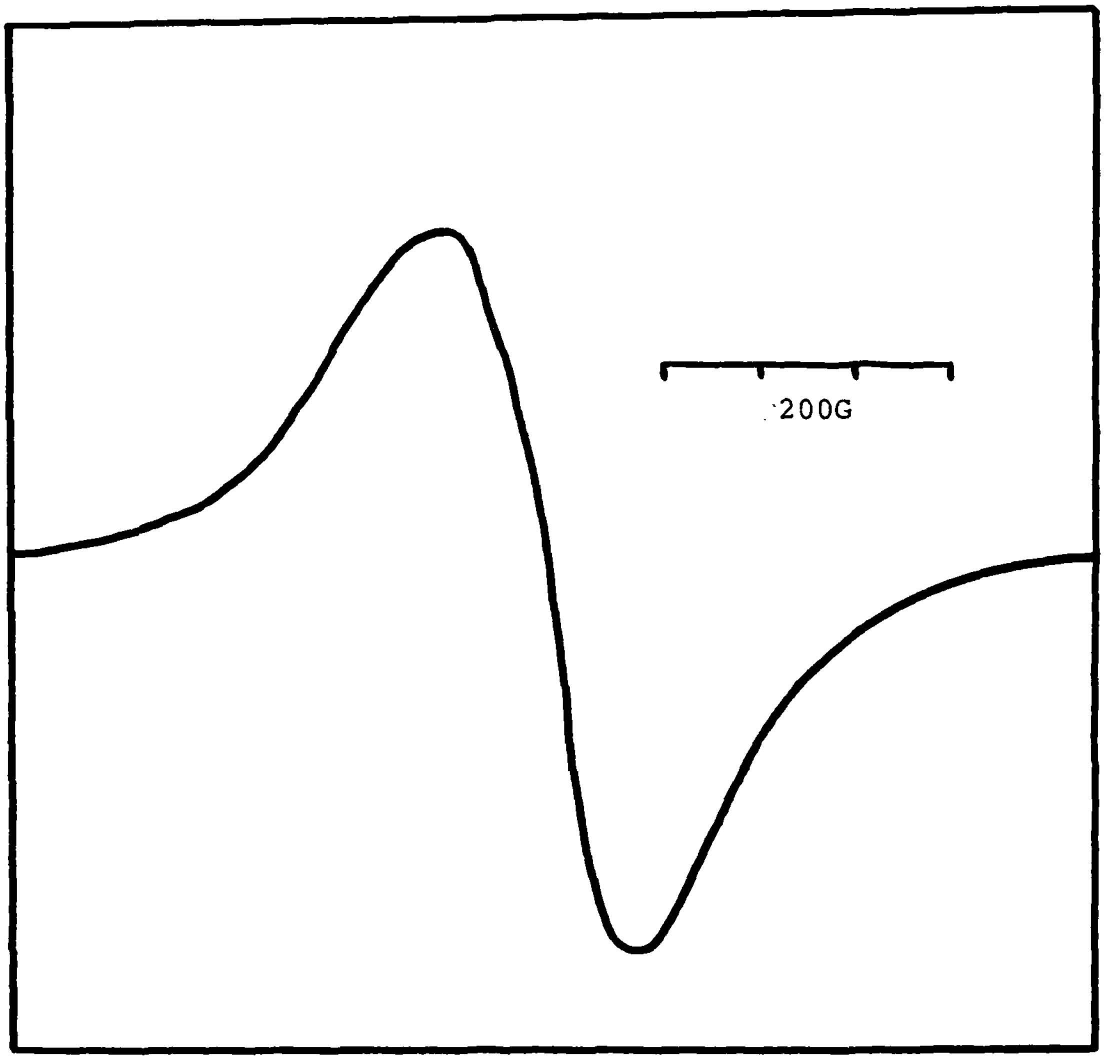

Figure 17: Electron spin resonance spectrum of ca. 9.7×10^{-3} M O_2^-/DMSO (field set = 2900 G)

$[SiW_{11}Cu(II)]^{6-}$ toluene solutions in a 1:1 stoichiometry. Two mL of 0.01 M $[SiW_{11}Cu(II)]^{6-}$/toluene (0.02 mmole) were placed in a 20 mL Ehrlenmeyer flask; 2.2 mL of ca. 8.7 x 10^{-3} M O_2^-/DMSO supernatant liquid was added by pipette. The flask was stoppered with a rubber septum and the solution stirred. The solution turned murky green-brown immediately (from the original aqua of the heteropolyanion). Stirring was continued for 24 hours with no change in color and an ESR spectrum was taken (Fig 18). Shown also in this figure are the spectra of the starting material (Spectrum A) and of the blank solution (Spectrum B). After 48 hours the solution was still green-brown and no precipitate was observed.

c) Reaction of O_2^- with $[SiW_{11}Cu(II)]^{6-}$ in Acetonitrile

The same procedure as above was followed. Freshly prepared 9.7 x 10^{-3} M O_2^-/DMSO (4.3 mL, 0.04 mmole) was added to 3.3 mL of 1.3 x 10^{-3} M $[SiW_{11}Cu(II)]^{6-}$/CH_3CN (0.04 mmole) in a 20 mL Ehrlenmeyer flask; the flask was stoppered and the solution stirred. The solution turned yellow-brown immediately. The solution was allowed to stand for 24 hours and the ESR spectrum taken (Fig 19). The solution color remained unchanged

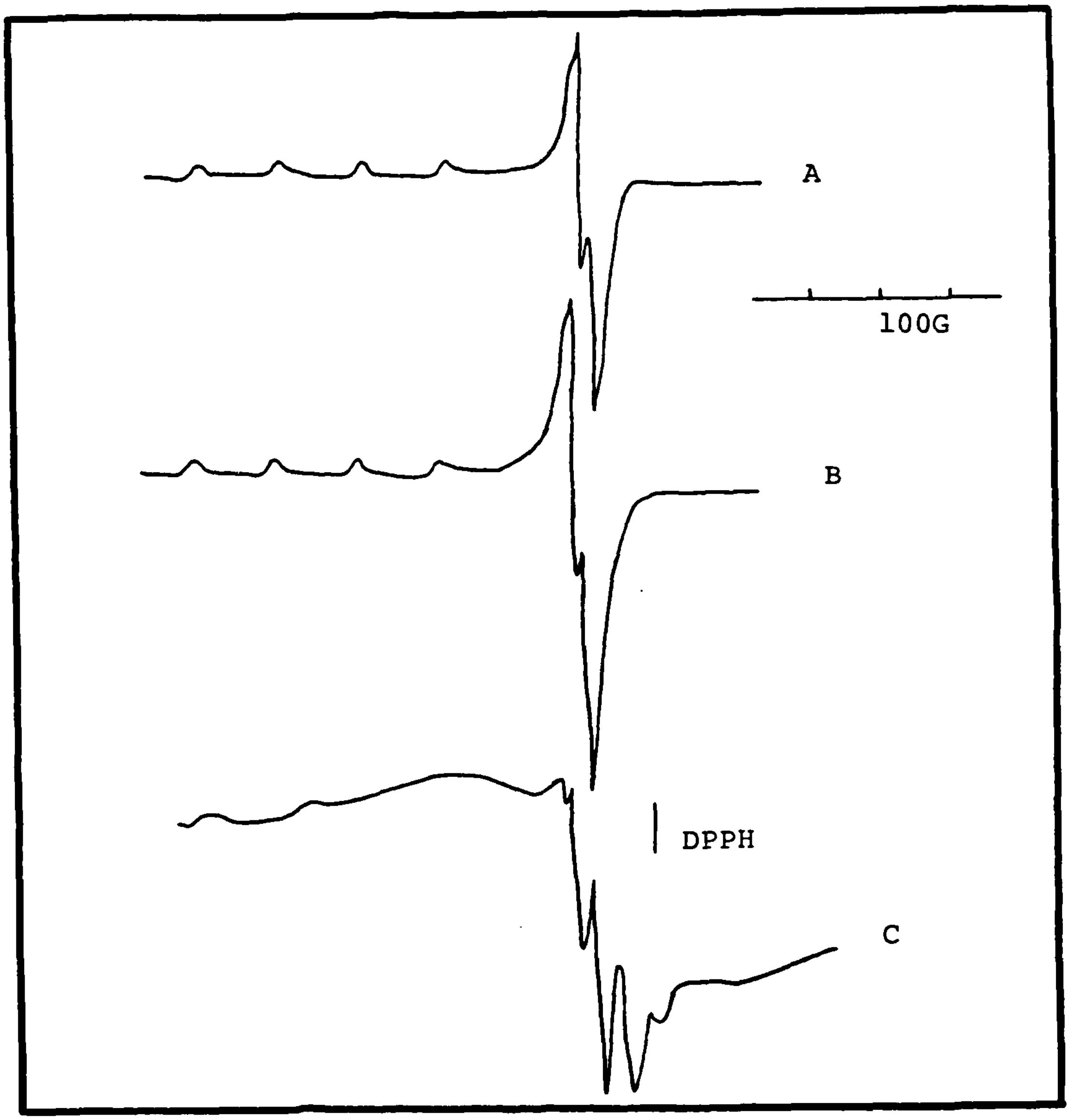

Figure 18: Electron spin resonance spectra of toluene solutions of (A) starting material, 0.01 M $[SiW_{11}Cu(II)]^{6-}$, (B) 0.01 M $[SiW_{11}Cu(II)]^{6-}$ with THpAB and DMSO (1:1), and (C) 0.01 M $[SiW_{11}Cu(II)]^{6-}$ after reaction with 9.7×10^{-3} M O_2^-/DMSO (field set = 2900 G)

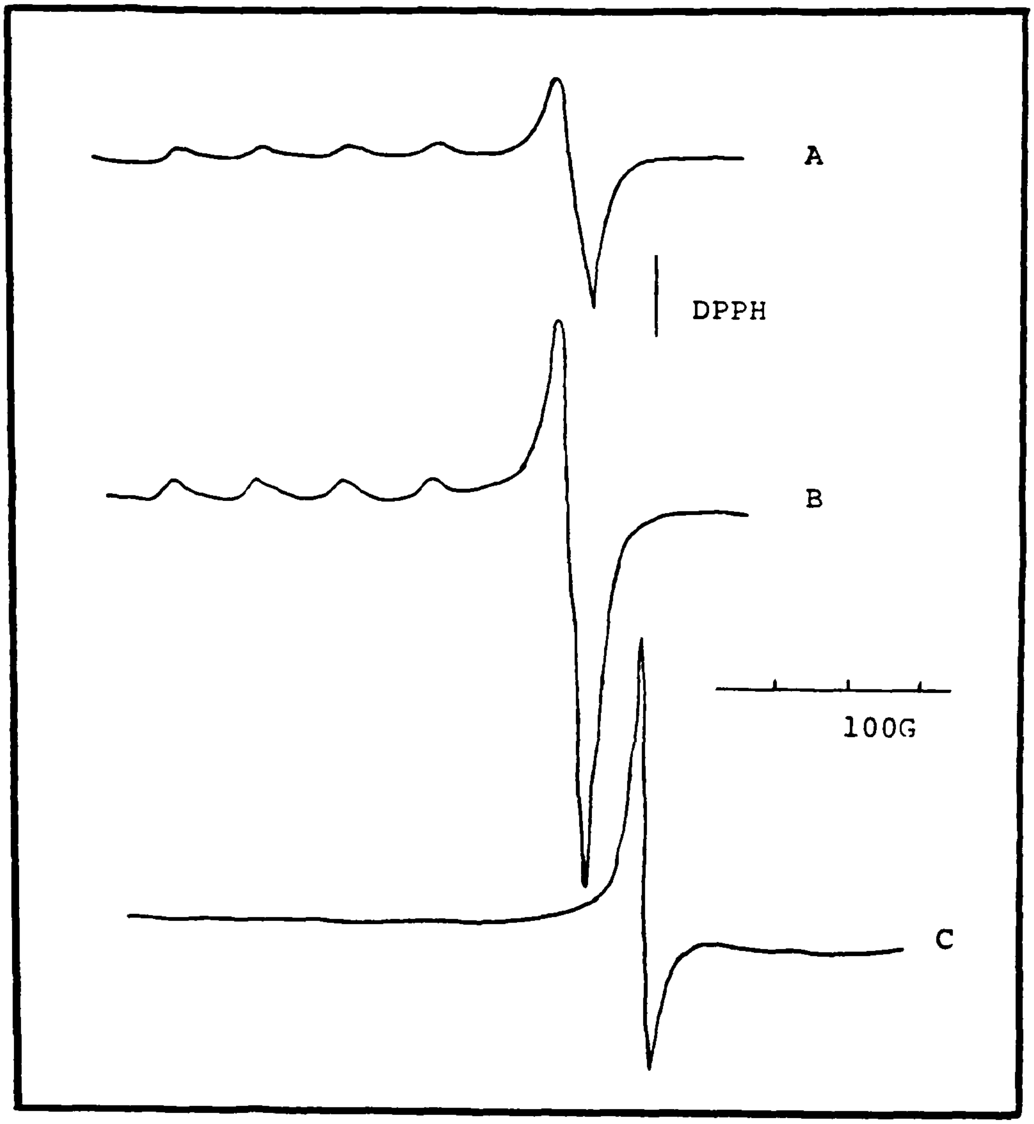

Figure 19: Electron spin resonance spectra of CH_3CN solutions of (A) starting material, 0.01 M $[SiW_{11}Cu(II)]^{6-}$, (B) 0.01 M $[SiW_{11}Cu(II)]^{6-}$ plus DMSO (1:1), and (C) 0.013 M $[SiW_{11}Cu(II)]^{6-}$ after reaction with 9.7×10^{-3} M O_2^-/DMSO (field set = 2900 G)

after 48 hours and no precipitate formed.

2) Discussion

a) Reaction of O_2^-/DMSO with $[SiW_{11}Cu(II)]^{6-}$ in Toluene

From the ESR spectrum of the green-brown reaction mixture in Fig 18, it is clear there is still Cu (II) in the product and that there is a mixture of ESR active products. Had reduction occured, an ESR spectrum would not be seen; Cu(I) is diamagnetic and therefore not ESR active. Many qualitative comparisons about this spectrum can be made. Although calculation of an accurate $g_\perp$ value is not possible, there is a visible shift of the perpendicular region toward DPPH (i.e. a decrease in the apparent $g_\perp$ value of 2.06 of the starting material to 2.04). This decrease toward 2.0037, the value of a free radical, indicates a shift of electron density away from copper to O_2^- so that its electronic structure resembles that of a free radical. The ESR spectrum indicates an interaction between O_2^- and Cu(II); how extensive the interaction is, if it actually constitutes a binding, is not yet answered. These values are consistent with reported $g_\perp$ values for biologial Cu(II) complexes[14.e] which range from 2.20 to 2.07. Another obvious change from the original material is the loss of structure in the parallel region. This may be due to unreacted O_2^- whose broad line would overlie this region (Fig 17).

Speculation can be made about the various products present remembering that Cu(II) must be present in all of them. There probably is unreacted starting material; the resemblance in both the appearance and position of the first two lines in Spectrum C to those of Spectrum A suggest this. A superoxide-copper(II) adduct could be present but with no electron transfer having occurred; the electron density having shifted from copper to superoxide. However, one might expect electron pairing between each of the unpaired electrons to make this species ESR inactive. Another possible structure is Cu(I)-O_2^{2-} adduct but this is not ESR active. Dicopper peroxide structures are known[30] (Cu_2O_2) and such a species could be envisioned: HPA_1-Cu(II)-O_2^--Cu(I)-HPA_2, where one copper atom has been reduced forming the peroxide; the peroxide is now stabilized by the two heteropolyanions. The basic result is that a single product does not form and clearly the reaction is not a simple one producing either the reduced or oxidized metal. From the spectroscopic data it cannot be said with certainity that O_2^- binds to copper(II) as a fifth ligand. Klug-Roth et al. have shown the reactivites of Cu(II) complexes toward O_2^- decrease when several ligand molecules (such as Cl^- and SO_4^{2-}) are attached to the copper atom[31]. The heteropoly pentadentate ligand may decrease the reactivity of copper and prevent actual binding of O_2^-.

One very important result from this experiment is seen in Spectrum B of Fig 18. This was the blank run prior to reaction with O_2^- to determine if DMSO binds as a fifth ligand. The spectrum shows no evidence of the fifth ligand. This is further supported by the near-IR spectrum which gives λ_{max} = 717 nm, the value identical to the ligand-off species.

Thus $[SiW_{11}Cu(II)]^{6-}$ in toluene has obviously undergone a change by reaction with O_2^-; but it was not completely reduced and the bonding of O_2^- as a fifth ligand can not be confirmed.

b) Reaction of O_2^-/DMSO with $[SiW_{11}Cu(II)]^{6-}$ in Acetonitrile

Figure 19 Spectrum C is the ESR of the yellow-brown reacted solution. The fact that an ESR spectrum is observed indicates the presence of Cu(II); the fact that the spectrum differs from that of the starting material implies the copper in the product is changed. The $g_\perp$ value decreases from 2.06 G in the original material to 1.99 G. Again there is the loss of structure in the parallel region. The single peak in the perpendicular region suggests only one product, a free radical-like structure. A possible species for the product could be the Cu(II)-O_2^- adduct. The adduct may form but reduction is not thermodynamically favored and electron transfer does not occur. The hyperfine structure of the parallel region would indicate the presence of a fifth ligand as in the case of the protonated heteropolyanion with a water molecule on the copper (Fig 13); without this hyperfine structure, it is impossible to determine if there is a fifth ligand or not.

As in toluene, a blank solution of ($[SiW_{11}Cu(II)]^{6-}$/THpAB/CH_3CN plus DMSO in a 1:1 ratio) was made to determine the effects of DMSO. As in toluene, the ESR spectrum (Spectrum B, Fig 19) did not show the characteristic spectrum of a fifth ligand on copper. The near-IR adsorbance showed a maximum absorbance at 727 nm, only slightly greater than the ligand-off value of 717 nm.

Thus, in a polar solvent, acetonitrile, the superoxide reaction produces a much simpler ESR spectrum, indicating the formation of one product. The product has a decreased $g_\perp$ value from that of the unreacted material. While excess O_2^-, which is a good base, may decompose the heteropolyanion, other reaction ratios where O_2^- is in slight excess may be worth investigating. Excess ligand may be required to find the copper(II) site and bind to it.

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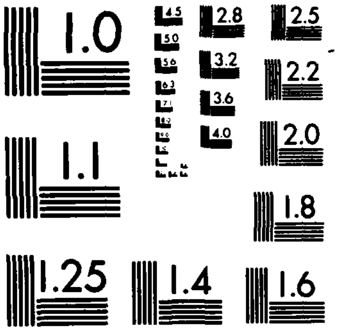

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BIOGRAPHY

The author was born in Columbus, Ohio, 15 May 53. She received her Bachelors degree in Chemistry from Miami University (Ohio) in May 77.

Upon graduation and commissioning in the United States Air Force, the author conducted research in solid rocket propulsion systems at the Rocket Propulsion Research Laboratory, Edwards Air Force Base, California. She has also been a Program Element Monitor (PEM) for both rocket propulsion programs and aerospace biotechnology Headquarters Air Force and Headquarters Air Force Systems Command.

With award of this degree the author will report for duty at the United States Air Force Academy, Colorado Springs, Colorado, as a chemistry instructor.

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