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Characterization of a Dimeric Copper(II) Complex of a Dissymmetric Schiff Base and Its Ligand Adducts[1a]

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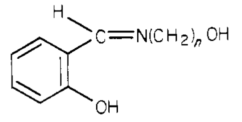
The synthesis and characterization of a binuclear copper(II) complex of a Schiff base derived from salicylaldehyde and (1*S*,2*S*)-$(+)_D$-1-phenyl-2-amino-1,3-propanediol are described. A distorted square-planar configuration about the copper centers is proposed on the basis of its spectral properties and its reduced magnetic moment in solution. The complex reacts in solution with a series of ligands to form bis(ligand) adducts in which the dimeric unit remains intact. The bis(imidazole) adduct exhibits catalase activity, and in the presence of hydrogen peroxide a band near 440 nm is observed that is most probably a O_2^{2-}–Cu(II) charge-transfer transition.

Introduction

Binuclear complexes of copper are currently of great interest because of the possibility of electronic interactions between the two metal centers[2] and also because of their relevance to the type 3, EPR silent, copper found in multicopper-containing proteins such as the hemocyanins, tyrosinase, and copper oxidases.[3] One of the distinguishing features of most dimeric complexes is a reduced magnetic moment resulting from either direct metal–metal interaction or interaction through a bridging ligand moiety. This feature can be related to the coordination geometry about the copper centers.[2,4] Schiff base complexes have been particularly valuable for designing complexes of widely differing structural types.[5-7] Complexes of Schiff bases prepared from salicylaldehyde and amino alcohols (I) have been prepared and well characterized.[8-12] These molecules can coordinate as a bi- or tridentate ligand by involving the alcohol group in the coordination sphere of the metal. The structures and magnetic properties of dimeric copper(II) complexes of these ligands $[CuSalN(CH_2)_nO]_2$ depend on *n*; complexes with $n = 2$ have been shown to be ferromagnetic and exhibit normal magnetic moments at room temperature. These complexes are believed to be tetrameric in the solid state on the basis of crystal structures reported for copper(II) complexes of Schiff bases formed from 2-aminoethanol and 2,4-pentanedione, $[Cu(acacNCH_2CH_2O)]_4$, and derivatives[12c,13] in which copper is in a pyramidal environment and each bridging oxygen is tetrahedrally bonded. On the other hand, complexes with $n = 3$ have reduced magnetic moments, and the copper atoms in the dimers are strongly antiferromagnetically coupled. The structures contain essentially planar configurations about the copper centers, and there is a relationship of decreasing strength of antiferromagnetic interaction with increasing distortion toward a tetrahedral configuration.[12b]



I

In the course of our study of complexes of Schiff bases, we have prepared a dimeric copper(II) complex of a Schiff base prepared from salicylaldehyde and the optically active amino alcohol (1*S*,2*S*)-$(+)_D$-1-phenyl-2-amino-1,3-propanediol, (+)-PAHPH,[14] which exhibited several unusual properties. Copper-containing proteins are agreed to contain the copper ions in dissymmetric ligand arrangements, and the elucidation of the structural aspects of these molecules is currently of great interest. Recent evidence has been given for the involvement of imidazole and phenoxide about the copper centers in oxyhemocyanins in a square-planar or square-pyramidal coordination geometry.[15,16] The prospect that the Schiff base with an optically active amino alcohol might induce significant dissymmetry in the complex led us to investigate the properties of this molecule. We report here the characterization of the complex and of several adducts formed with a series of nitrogen bases, including some imidazole derivatives.

Experimental Section

Materials. 1-Phenyl-2-amino-1,3-propanediol ligands, PAHPH (both the 1*S*,2*S* and 1*R*,2*R* entiomers), were obtained from Parke-Davis and Co. and were recrystallized to constant optical rotation, $[\alpha]_D$ ±27°, from either acetonitrile or ethanol. Imidazole was obtained from Eastman Chemicals, and its purity was ascertained by its UV absorption maximum, $\epsilon_{206} = 5100$.[17] Sublimation failed to yield any increase in the observed molar extinction coefficient. The 1-methyl- and 4-methylimidazole derivatives were obtained from Aldrich Chemical Co., and their stated purity (99%) was confirmed via ^1H

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(1) (a) Presented at the 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981. (b) Taken in part from the M.S. thesis of J. C. Brown.

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Table I. Solvent Dependence of the Absorption Spectrum of SalPAHP[a]

0.1 M HCl	H_2O[b]	CH_3OH	C_2H_5OH
		403 (sh)	
	395	400 (3.28)	405 (3.17)
342 (3.52)	325	315 (3.54)	316 (3.56)
280 (4.05)	280	280 (sh)	280 (sh)
260 (3.99)	255	255 (4.11)	255 (4.10)
206 (4.35)	210		

[a] λ, nm (log ε). [b] Spectrum determined on a saturated solution.

NMR spectroscopy. Both were used without additional purification. All other chemicals were of reagent grade quality and were used without additional purification.

Preparation of SalPAHPH. To a solution of 7.32 g (0.060 mol) of salicylaldehyde in 95% ethanol was added an ethanolic solution of 10.0 g of (+)-PAHPH (0.060 mol). The resulting mixture was refluxed for 5 min and allowed to cool to room temperature, and the yellow product was filtered and recrystallized from 95% ethanol: mp 188 °C; yield 11.0 g, 70%; mass spectrum, *m/e* 271 (M^+); $[\alpha]_D$ +259°. Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.8; H, 6.27; N, 5.17. Found: C, 70.8; H, 6.20; N, 5.00.

Preparation of the Copper Complex, $[CuSalPAHP]_2 \cdot H_2O$. A solution of copper(II) acetate monohydrate, 8.0 g (0.040 mol) in 170 cm^3 of water, was added to a solution of 10.9 g of SalPAHPH (0.040 mol) in 240 cm^3 of 95% ethanol. The resulting solution was treated with 40 g (0.5 mol) of sodium acetate dissolved in 200 cm^3 of water. The resulting mixture was heated to near boiling for 15 min and then allowed to cool to room temperature. The green product was filtered and recrystallized by dissolving in hot ethanol and adding water to induce precipitation; yield 6.7 g, 50%. An additional yield of 2.5 g was obtained from evaporation of the filtrate over several days time. Anal. Calcd for $Cu_2C_{32}H_{30}N_2O_6 \cdot H_2O$: C, 56.1; H, 4.67; N, 4.08; Cu, 18.5. Found: C, 56.3; H, 4.55; N, 4.06; Cu, 18.7.

Physical Measurements. Infrared spectra were obtained with use of potassium bromide pellets and Nujol mulls on Perkin-Elmer 521 and 621 infrared spectrophotometers. Electronic absorption spectra were recorded on a Cary 14 spectrophotometer or a Cary 17 spectrophotometer with a reflectance attachment. Magnetic susceptibility measurements were made at 30 °C (the normal NMR probe temperature) by using the NMR method of Evans[18] on a JEOL-C60-H NMR spectrometer. Corrections were made for the diamagnetic susceptibilities of the copper and the ligand atoms.[19]

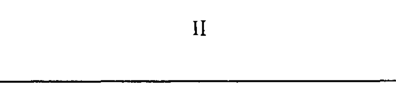
The elemental analysis and molecular weight determinations were performed by Galbraith Labs., Inc., Knoxville, TN.

The equilibrium constants for the formation of the adducts of bases with $[CuSalPAHP]_2 \cdot H_2O$ in ethanol were calculated from spectrophotometric measurements at fixed wavelengths in the visible spectral region. Absorbance changes with increasing base concentrations were monitored while the concentration of $[CuSalPAHP]_2 \cdot H_2O$ was kept constant at ca. 1.5×10^{-3} M. All solutions were prepared and all measurements were made in thermostated baths maintained at 25.0 ± 0.02 °C.

Reaction of the [CuSalPAHP]/imidazole system with hydrogen peroxide was studied spectrophotometrically in 60:40 ethanol:H_2O mixtures at 25 °C. Solutions containing ca. 1.00×10^{-3} M $[CuSalPAHP]_2 \cdot H_2O$ and a 5–10 molar excess of imidazole were treated incrementally with 0.05–0.5-mL portions of 1.0 M H_2O_2 prior to determination of the spectrum.

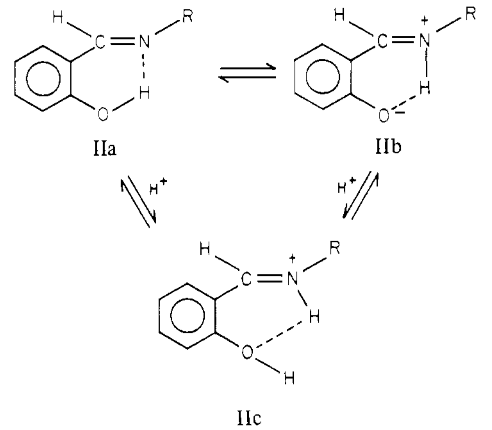
Results

The spectral and analytical results for the Schiff base ligand SalPAHP support the proposed structure, II. The mass spectrum of this molecule shows a molecular ion at *m/e* 271 corresponding to the calculated molecular weight of II. The infrared spectrum shows strong bands at 3400–3300 cm^{-1} in the O–H stretching frequency region and at 1645 cm^{-1}, which can be assigned to the imine stretch.[20] Two bands at 1609 and 1453 cm^{-1} correspond to bands assigned to aromatic carbon–carbon double-bond stretching frequencies. The ^1H NMR spectrum obtained in Me_2SO-d_6 also supports the structure with the methine hydrogen showing a singlet at 8.42 ppm.[20]



II

Scheme I



R = CH(CHOHPh)(CH_2OH)

Table II. Molecular Weight and Solution Magnetic Moments of $[CuSalPAHP]_2 \cdot H_2O$

solvent	mol wt	μ_{eff}, μ_B (303 K)
CH_2Cl_2	2273 (27 °C)	1.19
ETOH	887 (60 °C)	1.05

The electronic absorption spectrum of SalPAHPH in polar solvents is given in Table I. Schiff base ligands derived from salicylaldehyde and a primary amine are considered to exist predominantly in the enol–imine tautomeric form[5,20] although in polar solvents such as alcohols the spectral characteristics have been interpreted in terms of both the enol–imine and keto–enamine forms being present in solution,[21,22] with the two $\pi \rightarrow \pi^*$ transitions of each tautomer being observed. On this basis, the spectrum of SalPAHPH can be explained by assigning the bands at 315 and 255 nm to the enol–imine tautomer (IIa) and the bands at 400 and 280 nm to the keto–enamine form (IIb). In addition the bands near 210 and 255 nm probably contain the $\pi \rightarrow \pi^*$ transitions from the phenyl group on the amino alcohol portion of the ligand. In 0.1 M hydrochloric acid, the 400-nm band is not observed and a new band at 342 nm appears. The 400-nm band is responsible for the yellow color of Schiff bases and has been ascribed to the phenolate moiety in the keto–enamine form.[22] The 280-nm band, presumably associated with the imine grouping, would not be expected to shift significantly upon protonation, and no shift is observed. Other tautomers may also be present involving hydrogen bonding to the two alcohol functions. The pertinent equilibria are shown in Scheme I.

The molecular weight and magnetic moment of $[CuSalPAHP]_2 \cdot H_2O$ are shown in Table II along with the temperature at which they were measured. The reduced magnetic moments in both solvents indicate the presence of dimeric structures. The molecular weight in methylene chloride shows the complex to be associated. In methylene chloride the

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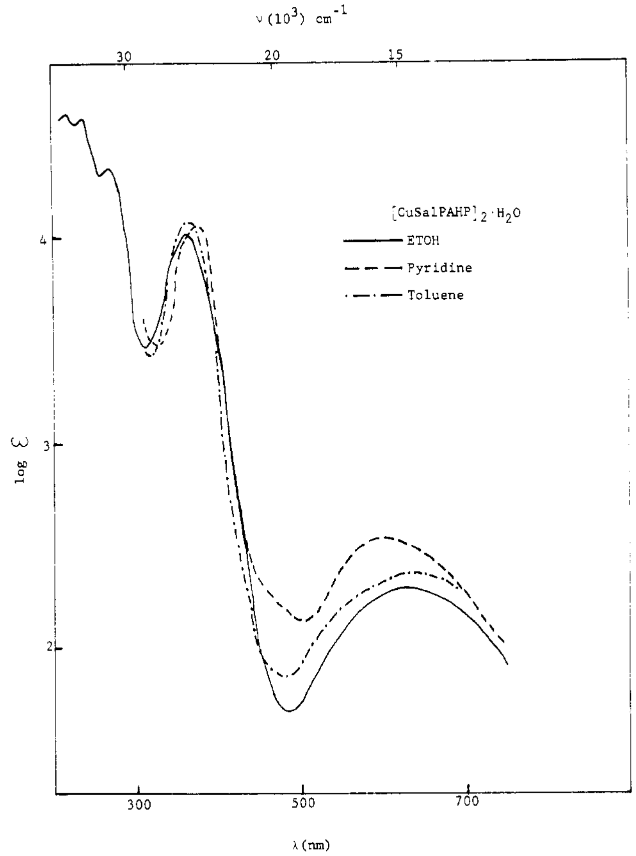

Figure 1. Absorption spectrum of $[CuSalPAHP]_2 \cdot H_2O$.

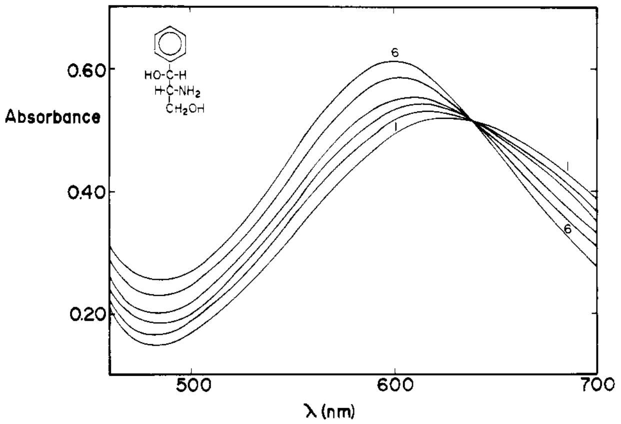

Figure 2. Absorption spectrum of $[CuSalPAHP]_2 \cdot H_2O$ (1.45×10^{-3} M) in the presence of (+)-PAHPH in ethanol. Concentrations of (+)-PAHPH: (1) 0; (2) 1.46×10^{-3} M; (3) 2.92×10^{-3} M; (4) 4.38×10^{-3} M; (5) 7.30×10^{-3} M; (6) 1.02×10^{-2} M.

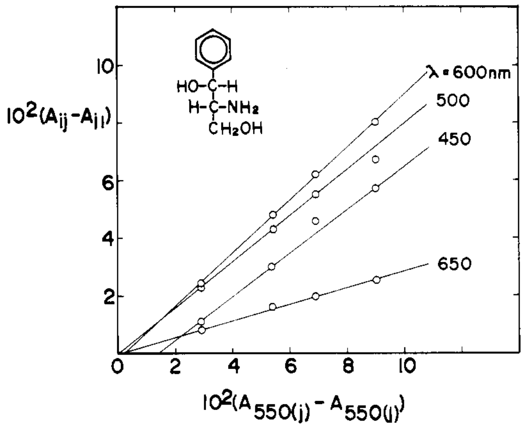

Figure 3. Test of spectral data for two absorbing species in the $[CuSalPAHP]_2 \cdot H_2O$–(+)-PAHPH system.

molecular weight measurements show a concentration dependence, and this coupled with spectroscopic results that show that Beer's law is not obeyed indicates the presence of a concentration-dependent equilibrium, most probably a partial dissociation of the associated species. In ethanol the molecular weight is more indicative of an unassociated dimeric species, although the observed value is still significantly higher than the calculated value of 683 for reasons that are not presently understood. The molecular weight measurements are invariant with concentration in ethanol and Beer's law is obeyed, which argues against any solvent-dependent equilibria in this solvent. The bulk of the data, including the results of the base adduct equilibria, discussed later, provide convincing evidence that in ethanol the unassociated dimer $[CuSalPAHP]_2$ is the principal species.

The absorption spectrum of $[CuSalPAHP]_2 \cdot H_2O$ (Figure 1) is seen to shift to shorter wavelengths with increasing solvent polarity; in toluene the maximum in the visible region occurs at 642 nm, which coincides with the reflectance spectrum, while in ethanol the band shifts to 627 nm and in pyridine the band appears at 597 nm. The band has a slight asymmetry, with a shoulder occurring on the high-energy side in ethanol and toluene and on the low-energy side in pyridine.

The solubility of this complex in a wide variety of solvents and the apparent accessibility of the copper centers to solvent coordination as indicated by the solvent dependence of the absorption spectra prompted a more detailed investigation of the interaction of a series of bases with $[CuSalPAHP]_2 \cdot H_2O$ in ethanol solution.

Significant spectral shifts were observed in the absorption spectrum of $[CuSalPAHP]_2$ in the presence of several coordinating ligands such as imidazole and (+)-PAHPH. The observation of an isosbestic point in each case near 635 nm suggested the presence of only two absorbing species up to a ligand to dimer ratio of about 5:1, above which no further spectral changes were observed. A typical series of spectra for (+)-PAHPH is shown in Figure 2. In addition, continuous variation experiments with both (+)- and (−)-PAHPH and imidazole gave a maximum absorbance at 2 mol of base per mol of dimer. To further test the spectral data, a graphical procedure[23] was employed based on the requirement that the order of the largest nonzero determinant in a matrix of absorbances A_{ij} for wavelength i and solution j is equal to the number of absorbing species in solution. For a series of solutions in which the total concentrations of absorbing species is kept constant, a plot of the absorbance differences ($A_{ij} - A_{i1}$) obtained by subtracting the absorbances for a single solution from the other absorbances at each wavelength vs. the differences at one wavelength should yield a family of straight lines passing through the origin for the case in which there are two absorbing species in solution. The results are shown for the ligand (+)-PAHPH in Figure 3. Equivalent results were obtained for each of the bases investigated.

The spectral data can be satisfactorily interpreted in terms of an equilibrium between $[CuSalPAHP]_2$ and a bis(ligand) adduct of the dimer (eq 1). The value of β_2 can be extracted

$$[CuSalPAHP]_2 + 2L \rightleftharpoons [CuSalPAHP(L)]_2 \quad \beta_2 \qquad (1)$$

from the spectral data. For a series of solutions, the absorbances at a given wavelength can be related to the concentrations of the absorbing species by the relation

$$\epsilon = \frac{A}{C_{Cu}} = \frac{A_{[Cu]} + A_{[CuL_2]}}{[Cu] + [CuL_2]} = \frac{\epsilon_0 + \epsilon_2\beta_2[L]^2}{1 + \beta_2[L]^2}$$

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Table III. β_2 Values for the Formation of Bis(ligand) Adducts in Ethanol at 25 ± 0.02 °C

L	$10^{-5}\beta_2$	L	$10^{-5}\beta_2$
ImH	2.12	pyz	18.5
1-MeIm	1.59	(+)-PAHP	1.65
4-MeIm	1.44	(−)-PAHP	1.70

Table IV. Magnetic Moments of Bis(ligand) Adducts of $[CuSalPAHP]_2$[a]

ligand	CH_2Cl_2	CH_3OH
ImH	1.16	0.93
1-MeIm	1.07	~1.0[b]
4-MeIm	1.07	1.03
pyz	0.76	0.50
(+)-PAHPH		0.92

[a] 303 K, in units of μ_B. [b] Crystallization occurs in this solvent.

In this expression, ϵ_0 and ϵ_2 are the molar extinction coefficients of $[CuSalPAHP]_2$ and the adduct, respectively, C_{Cu} is the total concentration of the copper-containing species, [Cu] represents the concentration of $[CuSalPAHP]_2$, and [L] is the equilibrium ligand concentration. Rearrangement of this equation gives a linear equation

$$\frac{\epsilon_0 - \epsilon}{\epsilon[L]^2} = \beta_2 - \frac{\epsilon_2\beta_2}{\epsilon}$$

so that a plot of $(\epsilon_0 - \epsilon)/\epsilon[L]^2$ vs. $1/\epsilon$ should give a linear plot with intercept β_2 and a slope of $-\epsilon_2\beta_2$.[24] The data were treated iteratively by calculating initial values for β_2 and ϵ_2 from the total ligand concentrations. The β_2 values so obtained were then used to calculate an average number of bound ligands, $\bar{n}$, and from this a new equilibrium ligand concentration was calculated. The β_2 values converged to a constant value after three cycles. The slope and intercept were evaluated by a linear least-squares regression calculation. The results of these calculations are shown in Table III. The calculated ϵ_2 values also obtained from these calculations were found to agree within ±1% of the experimentally determined values obtained from the spectra at high ligand concentrations. In addition, recalculation of absorbances from the resulting β_2 and [L] afforded values that agreed within ±0.5% of the experimental absorbances. At the lowest ligand concentrations, a consistently larger error (≤4%) suggested the presence of a 1:1 adduct. Experiments designed to measure a β_1 value, however, have been unsuccessful.

To confirm that $[CuSalPAHP]_2$ does not dissociate in the presence of high ligand concentrations, the magnetic moments of the $[CuSalPAHP(L)]_2$ adducts were determined in methylene chloride and methanol solutions in the presence of sufficient ligand to ensure complete adduct formation. The results are shown in Table IV. The reduced moments per copper atom confirm that the dimeric structure of $[CuSalPAHP]_2$ remains intact and provide confirming evidence for the equilibrium in eq 1. The spectral data for the bis(ligand) adducts are shown in Table V.

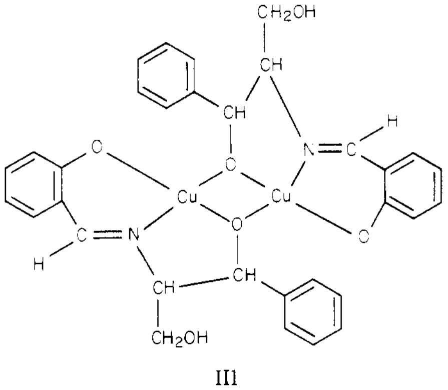
Discussion

The analytical and spectroscopic results for the free ligand SalPAHPH support the conclusion that the proposed structure II exists in the two tautomeric forms IIa and IIb in solution, and because the 400-nm band of the phenolate in IIc is the source of the yellow color, the keto–enamine form can also be supposed to be present in the solid state as well. The configuration of the amino alcohol used to prepare the Schiff base is *S*,*S*,[25] and since the Schiff base exhibits an optical rotation, it can be assumed that the configuration is retained upon formation of the Schiff base.

Table V. Absorption Spectral Data for Bis(ligand) Adducts $[CuSalPAHP(L)]_2$ in Ethanol

L	λ, nm (ε)	L	λ, nm (ε)
	626 (234)	pyz	560 (419)
ImH	570 (329)	(+)-PAHPH	596 (276)
1-MeIm	570 (328)	(−)-PAHPH	596 (276)
4-MeIm	572 (326)		

The copper complex was prepared from a water/ethanol solution of copper(II) acetate monohydrate and SalPAHP and was precipitated upon addition of sodium acetate as a base. The solubility of this complex in a wide variety of solvents prompted an investigation into the properties and reactions of this complex. The analytical, magnetic, and spectroscopic evidence can be explained in terms of the dimeric structure III with the Schiff base coordinating as a tridentate dinegative ligand. Whether the primary or secondary alcoholate is the coordinating species is as yet unknown; the parent (+)-PAHPH has been shown to bond through the secondary alcoholate group in two cases,[25,26] and on this basis it is assumed to be coordinated in this instance also. The bridging position for the alcoholate group is assigned on the basis of the position of the phenolic carbon–oxygen stretching frequency, which has been observed to shift from its position near 1540 cm^{-1} to higher frequencies for complexes with bridging phenolate moieties. On this basis, inspection of the carbon–oxygen stretch at 1535 cm^{-1} indicates a nonbridging phenolate ligand.



III

The reduced magnetic moment of $[CuSalPAHP]_2 \cdot H_2O$ in solution is consistent with the proposed dimeric structure. Previous studies on related complexes have shown for $[Cu(NRSal)]_n$ where R = CH_2CH_2O the structures are tetrameric in the solid state and have near normal magnetic moments, whereas complexes with R = $CH_2CH_2CH_2O$ have greatly reduced magnetic moments of 0.3–0.5 μ_B.[6] The tetrameric complexes are ferromagnetic and are believed to contain sp^3 hybridized bridging oxygen groups, in contrast to the antiferromagnetic complexes which are planar and allow antiferromagnetic coupling between the copper(II) ions via the oxygen bridges. The observed magnetic moment for $[CuSalPAHP]_2 \cdot H_2O$ of ca. 1.1 μ_B in a range of solvents such as ethanol, methylene chloride, and toluene suggests a planar structure with some tetrahedral distortion, in contrast to other R = CH_2CH_2O complexes. The SalPAHPH contains the bulky substituents C_6H_5 and CH_2OH, which may prevent a fully tetrahedral configuration about the copper atoms as is found in the tetrameric cases. Molecular weights measured in methylene chloride, Table II, indicate the presence of as-

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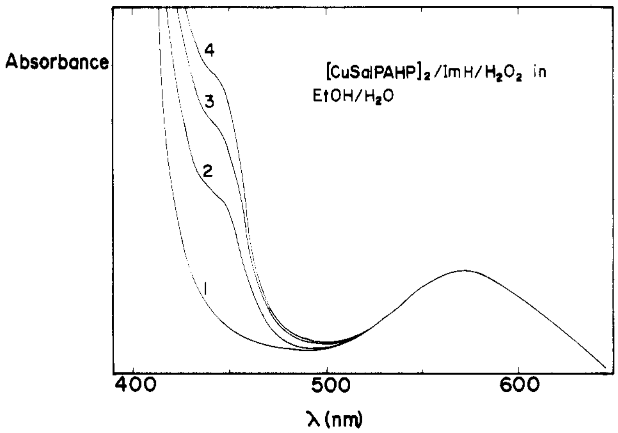

Figure 4. Absorption spectrum of the [CuSalPAHP]$_2$–imidazole system in the presence of increasing amounts of hydrogen peroxide (traces 1–4). Since the 440-nm band decreases with time, the H$_2$O$_2$ concentrations are relative only.

sociated species. The molecular weight data are concentration dependent, and this coupled with the fact that solutions of [CuSalPAHP]$_2$·H$_2$O in methylene chloride do not obey Beer's law suggests a concentration-dependent equilibrium, possibly a dissociation equilibrium.

The absorption spectrum of [CuSalPAHP]$_2$·H$_2$O (Figure 1) shows a single broad absorption band in the region of 620 nm. The band is solvent dependent, occurring at 640 nm in toluene (identical with the reflectance spectrum) and shifting to 626 nm in ethanol and 597 nm in pyridine. This solvent dependency is taken as evidence of solvent coordination to the copper. The position of the absorption maximum is consistent with a square-planar or a solvated square-pyramidal configuration about the coppers.[27] In pyridine, a shoulder is observed on the low-energy side typical of square-pyramidal copper complexes.[27] A slight but distinct shoulder is also seen on the high-energy side of the absorption band in toluene and ethanol. In at least one case, Cu((+)-PAHP)$_2$·H$_2$O, whose solid-state structure is known to be a square pyramid with an axially coordinated water molecule,[26] exhibits a band at 600 nm with a shoulder on the high-energy side at 525 nm. Thus the spectra in ethanol and toluene are consistent with solvent (or H$_2$O from the complex) coordination. No bands below 640 nm were observed, ruling out the possibility of tetrahedral species.[28]

The solubility characteristics of [CuSalPAHP]$_2$·H$_2$O and the availability of coordination sites on the copper ions in the complex suggested an examination of the reaction of this complex with a series of ligands. Because of the involvement of imidazole with type III copper in copper proteins, several imidazoles were included. Ethanol was chosen for the solvent, to permit a variety of ligands to be used. In ethanol, the molecular weight of 887 suggests a lower degree of association than in methylene chloride, although the observed value is still higher than the calculated value of 683 for reasons that are not presently understood. In contrast to methylene chloride, the molecular weight does not vary with concentration, and Beer's law is obeyed in ethanol. This coupled with the results of the equilibrium calculations with the various ligands (vide infra), which can be satisfactorily explained on the basis of only the unassociated dimer in solution, indicates the primary species is the unassociated dimeric complex.

Addition of the ligands to an ethanolic solution of [CuSalPAHP]$_2$·H$_2$O caused a shift in the copper d–d absorption band to higher frequencies (Figure 2) consistent with the development of a stronger ligand field about the copper, i.e., from a CuNO$_3$ donor set to a CuN$_2$O$_3$ donor set. The results of the equilibrium calculations provide good evidence for the 1:2 ligand adducts being the major product formed under these conditions. Presumably one ligand coordinates to each copper in the dimer, creating a five-coordinate square-pyramidal coordination geometry. The reduced moments measured in the presence of excess ligand confirm that the dimeric structure remains intact. The β_2 values (Table III) show little relationship to base strength of the ligands; the similarity of the values for imidazole, 2-methylimidazole, and 4-methylimidazole suggests all three coordinate through the same nitrogen donor, which must be the imine nitrogen in the case of the 1-methyl derivative.[31] The lowest value is observed for the 4-methylimidazole, which may reflect some steric hindrance of the methyl group. Similar β values are also found for the complexation of copper(II) ion with these three ligands.[29] A surprising result is the much greater β_2 value for pyrazole, which normally is considered to a weaker ligand than imidazole.[30] This enhanced stability may reflect bridging of the pyrazole (pyz) between the two coppers of the dimer. Stronger chelating ligands such as 8-hydroxyquinoline were found to disrupt the dimer, forming β-bis(8-hydroxyquinolinato)copper in about 80% yield. In keeping with this, in a preparative reaction of pyrazole and [CuSalPAHP]$_2$·H$_2$O the product obtained was Cu$_3$(SalPAHP)$_2$(pyz)$_2$·6H$_2$O, indicating at least partial breakup of the dimer.

One especially intriguing aspect of the bis(imidazole) adduct is its observed catalase activity. In aqueous ethanol solution hydrogen peroxide is catalytically decomposed. Addition of hydrogen peroxide also results in the formation of a spectrum (Figure 4) very similar to that of oxyhemocyanin,[15,16,32] with a band at 570 nm and a new band near 440 nm, which decays to give the original spectrum of the adduct as decomposition of H$_2$O$_2$ proceeds. The band may be regenerated for several cycles by the addition of more H$_2$O$_2$. Bands have been observed in this region in the spectra of octopus oxyhemocyanin[16] and have been assigned to an O$_2^{2-}$–Cu charge-transfer bond[15,31] or a phenoxide–copper charge-transfer bond.[16] In the present case it seems likely that the 440-nm band is due to an O$_2^{2-}$–Cu(II) CT band as the constancy of the 570-nm band throughout the formation and decay of the 440-nm band can be taken to indicate there is no significant change in coordination geometry or bonding that might give rise to a new phenoxide–copper CT band. This reaction is currently being studied and will be reported in a later publication.

Registry No. [CuSalPAHP]$_2$, 80327-02-2; SalPAHPH, 80301-54-8; [CuSalPAHP(ImH)]$_2$, 80327-08-8; [CuSalPAHP(1-MeIm)]$_2$, 80327-07-7; [CuSalPAHP(4-MeIm)]$_2$, 80327-06-6; [CuSalPAHP(pyz)]$_2$, 80327-05-5; [CuSalPAHP((+)-PAHPH)]$_2$, 80374-40-9; [CuSalPAHP((−)-PAHPH)]$_2$, 80327-04-4; CuSalPAHP(1-MeIm), 80327-03-3; salicylaldehyde, 90-02-8; (+)-PAHPH, 28143-91-1.

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(31) Recent results of an X-ray crystallographic structure determination of the crystalline material obtained from methanol solutions of the 1-MeIm adduct (Table IV) have shown this material to be a monomeric square-planar copper(II) complex, Cu(SalPAHP)(1-MeIm), which has been found to have a normal magnetic moment of 1.84 μ_B in the solid state: Sinn, E., private communication. The SalPAHP ligand is coordinated to the copper via the salicylaldehyde portion and the secondary alcoholate moiety as proposed. In ethanol solution in the presence of excess 1-MeIm, this complex shows identical spectral properties and reduced magnetic moment with those reported in this work, indicating the same species are present in solution.

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