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Binuclear Metal Complexes. 2. A Unique Mononuclear Copper(I) Complex with a Potentially Binucleating Schiff Base Ligand

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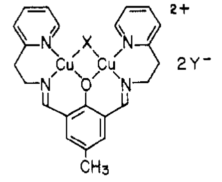
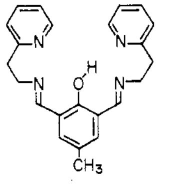
The attempted synthesis of binuclear copper(I) complexes with the binucleating Schiff base ligand $(AEP)_2IPAH$ derived from the condensation of 2-hydroxy-5-methylisophthalaldehyde and 2-(2-aminoethyl)pyridine leads to the isolation of the mononuclear complexes $[Cu^I(AEP)_2IPAH]Cu^ICl_2$ and $[Cu^I(AEP)_2IPAH]BF_4$. Analytical data and spectral and magnetic studies support the proposed formulations of these complexes. The intense visible absorption band for the cation $[Cu^I(AEP)_2IPAH]^+$ is attributed to an intraligand $\pi \rightarrow \pi^*$ transition within a keto amine tautomer of the Schiff base ligand which is stabilized by coordination with copper(I). $[Cu^I(AEP)_2IPAH]^+$ reacts reversibly with carbon monoxide in acetonitrile or dimethyl sulfoxide solution at room temperature to form a terminally bonded CO adduct (ν_{CO} = 2075 cm^{-1}). The copper(I) complexes are very sensitive toward oxygen, and air oxidation of $[Cu^I(AEP)_2IPAH]Cu^ICl_2$ leads to the binuclear copper(II) complex $[Cu_2(AEP)_2IPA(OH)]Cl_2$, similar to those reported previously.

Introduction

Recent interest[1-4] in the redox behavior of binuclear copper chelates stems from the suggestion that the oxidized form of type 3 (ESR nondetectable) copper in various copper-containing proteins occurs as binuclear copper(II) centers.[5-7] These antiferromagnetically coupled dicopper(II) centers provide 2 oxidizing equiv in the redox activity of laccase[8] and may function similarly in ceruloplasmin[7,9,10] and ascorbate oxidase.[7] In a previous paper[1] we described a series of dicopper(II) complexes, including **1**, with four new binucleating Schiff base ligands derived from 2-hydroxy-5-methylisophthalaldehyde. Binucleating ligands based on this dialdehyde were introduced by Robson[11] and Okawa and Kida[12] and have been extensively investigated by these groups. The electrochemical behavior of **1** and related analogues was highly irreversible, and we were not able to prepare the mixed-valence or dicopper(I) analogues by controlled-potential electrolyses for the complexes containing chloride or hydroxide bridging groups.

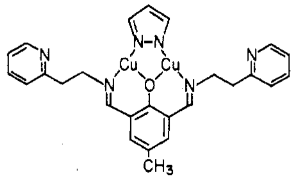


$[(Cu_2(AEP)_2IPA)X]Y_2$
1a, X = Y = Cl$^-$
b, X = OH$^-$; Y = ClO$_4^-$



$(AEP)_2IPAH$
2

We report here the direct synthesis of copper(I) derivatives with the binucleating ligand **2** derived from 2-hydroxy-5-methylisophthalaldehyde and 2-(2-aminoethyl)pyridine. Binuclear copper(I) complexes were not achieved; however, a unique mononuclear copper(I) complex with the binucleating ligand was isolated and characterized. During our investigation, Gagné and coworkers[13] reported that the complex $[Cu_2^{II}(AEP)_2IPA(pz)]^{2+}$, **1**, X = pz = pyrazolate, exhibits two quasi-reversible one-electron reductions at more positive potentials than those we observed for the chloride- and hydroxide-bridged analogues. Subsequently, pyrazolate-bridged binuclear Cu(I) complexes were isolated with deprotonated **2** and a large number of analogs and were shown to have the three-coordinate structure represented by **3**. These binuclear Cu(I) complexes, stabilized by the bridging heterocycle anion pyrazolate, provide an interesting contrast to our complexes since they exhibit significantly different chemical behavior than the mononuclear species reported here.



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Experimental Section

Materials. Benzylamine (Matheson Coleman and Bell), 2-(2-aminoethyl)pyridine (Aldrich Chemical Co.), and 2,2′-biquinoline (G. F. Smith and Co.) were used as received. The dialdehyde, 2-hydroxy-5-methylisophthalaldehyde (IPAH), was prepared by the method of Ullman and Brittner.[14] Cuprous chloride (J. T. Baker Co.; 90% Cu(I)) was purified by the method of Keller and Wycoff[15] and stored in a desiccator. Tetrakis(acetonitrile)copper(I) fluoroborate, $Cu(CH_3CN)_4BF_4$, was synthesized by a variation of the literature procedure for $Cu(CH_3CN)_4ClO_4$.[16] All other chemicals were reagent grade or better and were used as received.

Ligands. All attempts to isolate the free ligand 2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol, **2** ($(AEP)_2IPAH$), prepared from the condensation of 2 mol of 2-(2-aminoethyl)pyridine and 1 mol of 2-hydroxy-5-methylisophthalaldehyde, yielded orange oils which could not be induced to crystallize.

2-[*N*-(2-Pyridylethyl)iminomethyl]-6-formyl-4-methylphenol, (AEP)IPAH, 4. A mono(Schiff base) ligand is prepared by combining

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0.41 g (2.5 mmol) of IPAH in 25 ml of cyclohexane with 0.30 g (2.5 mmol) of 2-(2-aminoethyl)pyridine and distilling off the water of condensation as an azeotrope. The yellow solid which forms on cooling is collected and recrystallized from a 1% acetonitrile in cyclohexane solution. The resulting yellow crystals are vacuum dried at 65 °C; mp 96–98 °C. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.80; H, 6.20; N, 10.62.

2,6-Bis(*N*-benzyliminomethyl)-4-methylphenol, $(BZA)_2$IPAH, 5. A cyclohexane solution (15 mL) of 0.41 g (2.5 mmol) of IPAH is combined with 0.54 g (5.0 mmol) of benzylamine, and the water of condensation is removed via an azeotrope during 1 h of reflux. The orange microcrystalline product which forms upon cooling to 0 °C is recrystallized from cyclohexane and dried in vacuo at room temperature; mp 68–72 °C. Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48; N, 8.18. Found: C, 80.46; H, 6.32; N, 8.06.

Metal Complexes. [2,6-Bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol]copper(I) Dichlorocuprate(I), $[Cu(AEP)_2IPAH]CuCl_2$, 6a. This synthesis is carried out in Schlenk glassware under an atmosphere of purified nitrogen. To 0.5 g (5.0 mmol) of $CuCl_2$ dissolved in 20 mL of acetonitrile is added slowly a solution of 0.41 g (2.5 mmol) of IPAH and 0.6 g (5.0 mmol) of 2-(2-aminoethyl)pyridine in 10 mL of acetonitrile. The resulting dark red solution is warmed to 50 °C and filtered to remove any undissolved reactants. The filtrate is cooled overnight at 0 °C, yielding a dark red crystalline product which may be recrystallized from warm acetonitrile to give an orange microcrystalline solid. The product is collected, dried in vacuo at room temperature, and stored in an inert-atmosphere box. Anal. Calcd for $C_{23}H_{24}N_4OCu_2Cl_2$: C, 48.43; H, 4.24; N, 9.84; Cl, 12.43. Found: C, 48.41; H, 4.19; N, 9.90; Cl, 12.53.

[2,6-Bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol]copper(I) Tetrafluoroborate, $[Cu(AEP)_2IPAH]BF_4$, 6b. This complex is prepared in the same manner as is $[Cu(AEP)_2IPAH]CuCl_2$ by substituting $Cu(CH_3CN)_4BF_4$ as the source of Cu(I) ion and using smaller volumes of acetonitrile. Red crystals of $[Cu(AEP)_2IPAH]BF_4{\cdot}xCH_3CN$ are isolated. The solvate molecules are lost upon drying in vacuo at room temperature, yielding an orange powder. Anal. Calcd for $C_{23}H_{24}N_4OCuBF_4$: C, 52.84; H, 4.63; N, 10.72; F, 14.54. Found: C, 52.64; H, 4.77; N, 10.73; F, 14.31. This complex can also be prepared in methanol solution. The crude precipitate is filtered quickly to minimize disproportionation and is recrystallized from 9:1 (v/v) methanol–acetonitrile to yield red crystals. Upon drying in vacuo at room temperature, these crystals break down to an orange powder identical with that prepared from acetonitrile solution.

[2,6-Bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol]copper(I) Carbonyl Tetrafluoroborate, $[Cu(AEP)_2IPAH(CO)]BF_4{\cdot}xCH_3CN$. This carbonyl adduct is prepared by concentrating a solution of $[Cu(AEP)_2IPAH]BF_4$ (0.5 g in 15 mL of CH_3CN) under N_2 to the point where crystallization is incipient and exposing the solution to an atmosphere of CO. The CO (Air Products Technical Grade), which has been passed through a column of BASF catalyst to remove residual O_2, is introduced into the flask via a series of CO/vacuum cycles. The dark red solution quickly becomes yellow. The mixture is gently heated under the 1 atm of CO to redissolve any complex which may have precipitated. The reaction mixture is kept at −10 °C overnight, and the yellow crystals which form are collected under a positive pressure of CO by using Schlenk techniques. These crystals are "dried" by passing a stream of CO through the Schlenk filtration flask. The dried crystals are stored under an atmosphere of CO at 0 °C. Owing to the lability of the CO adduct, analytical data could not be obtained. The carbonyl adduct, $[Cu(AEP)_2IPAH(CO)]CuCl_2$, is prepared in an analogous manner.

Physical Measurements. Galbraith Laboratories, Inc., Knoxville, Tenn., provided the elemental analyses. Infrared spectra, electronic absorption spectra, and room-temperature magnetic susceptibilities were determined as described previously.[1] Spectrophotometric titrations of air-sensitive samples were carried out in a special cell consisting of a one-neck (14/20) 25-mL bulb to which an optical cell is attached. The titration cell is filled in an inert atmosphere with a known volume of solution and sealed off with a rubber septum. Titrant is added via an airless syringe which has been filled in an inert atmosphere.

Results and Discussion

The binuclear copper(II) complexes **1**, and related analogues containing chloride or hydroxide bridging groups, exhibit irreversible electrochemical behavior and could not be converted to mixed-valence or binuclear copper(I) derivatives by controlled-potential electrolyses.[1] We therefore attempted to synthesize copper(I) complexes of these ligands directly by the reaction of a source of copper(I) ions with ligand solutions generated in situ. When $Cu(CH_3CN)_4BF_4$ reacted with **2** in acetonitrile, deep red crystals were isolated which readily lost CH_3CN under vacuum to yield an orange powder with the composition $[Cu(AEP)_2IPAH]BF_4$, where $(AEP)_2$IPAH represents the binucleating ligand **2** without the loss of the phenolic proton. The presence of the protonated form of the ligand is confirmed by a broad absorption at 2200 cm^{-1} in the infrared spectrum of the deuterated complex $[Cu(AEP)_2IPAD]BF_4$, prepared by recrystallization of the complex from methanol-d_1. Reactions with $Cu(CH_3CN)_4BF_4$:ligand ratios of 2:1 or greater also only yielded the mononuclear complex.

Table I. Electronic Spectral Data for the Cu(I) Complexes of $(AEP)_2$IPAH

compd	solvent	ν_{max}, cm^{-1} (ϵ)
$[Cu(AEP)_2IPAH]BF_4$	solid state (KBr)	22 600
	dimethyl sulfoxide	22 600 (8000)
	methanol	22 700 (8800)
	acetonitrile	22 400 (4500), 28 300 (5300)
$[Cu(AEP)_2IPAH]CuCl_2$	solid state (KBr)	22 400
	dimethyl sulfoxide	22 600 (7600)
	methanol	$CuCl_2^-$ disproportionates
	acetonitrile	22 300 (4000), 28 300 (5400)

The reaction of 2 mol of cuprous chloride with 1 mol of the binucleating ligand in acetonitrile leads to the isolation of red crystals which are formulated as $[Cu(AEP)_2IPAH]CuCl_2$ on the basis of elemental analyses and by analogy to the fluoroborate salt. An alternative formulation of this complex as a binuclear species, $[Cu_2(AEP)_2IPA]Cl_2$, differs only by one proton in composition but implies a mixed-valence description of the two copper ions from the required charge balance of three uninegative ligands. Since $[Cu(AEP)_2IPAH]CuCl_2$ exhibited none of the magnetic properties anticipated for a mixed-valence species (see below), this formulation was rejected. The close agreement of the infrared and optical spectra of $[Cu(AEP)IPAH]BF_4$ and $[Cu(AEP)IPAH]CuCl_2$, described in detail below, supports their formation as mononuclear copper(I) cationic complexes differing only in the nature of the counterion.

All attempts to react solutions of the binucleating ligand **2** in acetonitrile or methanol with cuprous chloride or $Cu(CH_3CN)_4BF_4$ in the presence of a base (triethylamine or sodium methoxide) in order to deprotonate the ligand resulted in disproportionation of the Cu(I) as evidenced by the deposition of elemental copper. It could not be ascertained whether the disproportionation occurred as a result of a phenolato-bridged dicopper(I) complex with the binucleating ligand or simply by interaction of the base with the cuprous reagent.

Magnetic and Spectral Properties. Both $[Cu(AEP)_2IPAH]BF_4$ and $[Cu(AEP)_2IPAH]CuCl_2$ are diamagnetic as determined by room-temperature magnetic susceptibility measurements, and neither complex exhibits any electron spin resonance signals in agreement with their formulation as cuprous species. The essentially identical spectral behavior (Table I and Figure 1) of these two complexes in various solvents provides the strongest evidence that they both contain the $[Cu(AEP)_2IPAH]^+$ cation and differ only in the nature of the anion. The spectra of both complexes in the solid state (diffuse transmittance) or in Me_2SO solution exhibit an intense band at ~22 600 cm^{-1}. In methanol, the same spectrum is obtained for $[Cu(AEP)_2IPAH]BF_4$ but $[Cu(AEP)_2IPAH]CuCl_2$ disproportionates owing to an instability

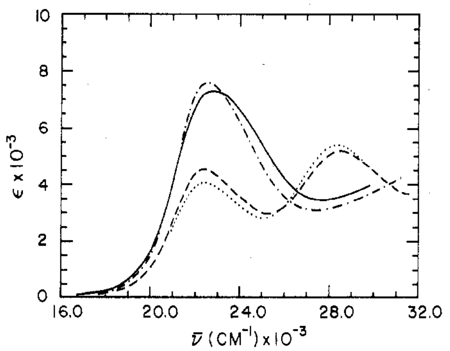


Figure 1. Absorption spectra of $[\mathrm{Cu(AEP)_2IPAH}]\mathrm{BF_4}$ in $\mathrm{Me_2SO}$ (—) and acetonitrile (---) and $[\mathrm{Cu(AEP)_2IPAH}]\mathrm{CuCl_2}$ in $\mathrm{Me_2SO}$ (-··-) and acetonitrile (···).

Table II. Solvent Dependence of the Electronic Spectra of the Schiff Bases (AEP)IPAH and $(\mathrm{BZA})_2\mathrm{IPAH}$

solvent	dielectric const[a]	$\nu_{\max}$, cm^{-1} (ϵ) (AEP)IPAH	$\nu_{\max}$, cm^{-1} (ϵ) $(\mathrm{BZA})_2\mathrm{IPAH}$
cyclohexane	2.023[a]	28 200 (6700)[b]	28 300 (7700)[b]
chloroform	4.806[a]	28 100 (5300),[b] 22 100 (830)[c]	28 300 (7600),[b] 22 400 (300)[c]
methanol	32.63[a]	28 100 (3900),[b] 22 400 (3800)[c]	28 500 (6100),[b] 22 500 (2300)[c]
acetonitrile	37.5[d]	28 100 (4900),[b] 22 000 (2800)[c]	28 500 (6900),[b] 22 400 (400)[c]

[a] Value taken from: "CRC Handbook of Chemistry and Physics", 50th ed.; CRC Press, Boca Raton, Fla., 1969; p E-62. [b] Assigned to the enol imine tautomer. [c] Assigned to the keto amine tautomer. [d] Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Interscience: New York, 1970; p 400.

of the $\mathrm{CuCl_2}^-$ anion in this solvent. In acetonitrile solution, both complexes exhibit a band at ~22 400 cm^{-1} with diminished intensity and a new band at 28 300 cm^{-1} which is not observed in other solvents. This behavior is interpreted as a competition between the binucleating ligand and acetonitrile for coordination of the Cu(I) according to the equilibrium

$$[\mathrm{Cu(AEP)_2IPAH}]^+ + \mathrm{CH_3CN(excess)} \rightleftharpoons (\mathrm{AEP})_2\mathrm{IPAH} + [\mathrm{Cu(CH_3CN)}_n]^+ \quad (1)$$

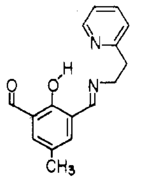
The decrease in the 22 400-cm^{-1} band represents a lowered concentration of $[\mathrm{Cu(AEP)_2IPAH}]^+$, and the 28 300-cm^{-1} band is attributed to the free ligand. This equilibrium is reasonable in light of the known affinity of Cu(I) for acetonitrile[16,17] and from evidence described below that similar Schiff bases of 2-hydroxy-5-methylisophthalaldehyde exhibit a major absorption band at ~28 300 cm^{-1}.

Three lines of evidence further confirm the existence of the proposed equilibrium represented by (1). First, the addition of a large excess of $\mathrm{Cu(CH_3CN)_4BF_4}$ to an acetonitrile solution of $[\mathrm{Cu(AEP)_2IPAH}]^+$ produces a dramatic increase in the 22 400-cm^{-1} band while the 28 300-cm^{-1} band disappears. Thus excess Cu(I) forces the formation of $[\mathrm{Cu(AEP)_2IPAH}]^+$. The anomalously high extinction coefficient ($\epsilon \approx 12\,000$ L mol^{-1} cm^{-1}) for the 22 400-cm^{-1} band at a Cu(I):ligand ratio of 25:1 may represent the formation of a complex species with greater than a 1:1 stoichiometry. No breaks in the absorbance vs. mole ratio curves were observed at 2:1 Cu(I):ligand, however, and no binuclear species could be isolated from these solutions. The large excess of $\mathrm{Cu(CH_3CN)_4BF_4}$ needed to achieve constant values of $\epsilon_{\max}$ suggests that the binucleating ligand **2** has little tendency to bind two Cu(I) ions.

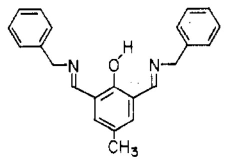
Further evidence for the proposed equilibrium in acetonitrile solution is provided by competitive binding studies between $(\mathrm{AEP})_2\mathrm{IPAH}$ and 2,2′-biquinoline, a copper(I) specific reagent.[18] The addition of 2,2′-biquinoline to a methanol solution of $[\mathrm{Cu(AEP)_2IPAH}]^+$ produces a new band at 18 300 cm^{-1} characteristic of Cu(2,2′-biquinoline)$_2^+$ together with a corresponding decrease in the $[\mathrm{Cu(AEP)_2IPAH}]^+$ band at 22 600 cm^{-1}. In acetonitrile solution the 18 300-cm^{-1} band appears without any decrease in the 22 400-cm^{-1} band, indicating that this band arises predominantly from the free ligand $(\mathrm{AEP})_2$IPAH predicted by equilibrium 1. The behavior of the 28 300-cm^{-1} band is masked by an intense absorption of Cu(2,2′-biquinoline)$^+$. That equilibrium 1 lies far to the right is further confirmed by the similarity of the spectra for $(\mathrm{AEP})_2$ IPAH and $[\mathrm{Cu(AEP)_2IPAH}]^+$ in acetonitrile solution as discussed below (cf. Tables I and II). The formation of the Cu(2,2′-biquinoline)$_2^+$ complex in an acetonitrile solution of $[\mathrm{Cu(AEP)_2IPAH}]^+$ therefore occurs with the solvated Cu(I) ions predicted by equilibrium 1.

In a similar experiment the addition of acetonitrile to a methanol solution of $[\mathrm{Cu(AEP)_2IPAH}]\mathrm{BF_4}$ produces the same effect on the 22 600-cm^{-1} band as does the addition of 2,2′-biquinoline. In a 50:50 mixture of acetonitrile and methanol by volume, the band at 22 600 cm^{-1} is diminished (ϵ = 4500), while the free-ligand band at 28 400 cm^{-1} is increased (ϵ = 4900).

Several lines of investigation were pursued to elucidate the origin of the 22 600-cm^{-1} band of $[\mathrm{Cu(AEP)_2IPAH}]^+$ and to provide evidence for the coordination mode in this complex ion. First, the optical spectra of Schiff bases derived from 2-hydroxy-5-methylisophthalaldehyde were studied. Since all attempts to isolate **2** resulted in the formation of a viscous oil, two analogues of the free ligand were utilized for the spectroscopic studies. These two compounds, the monocondensed Schiff base, (AEP)IPAH, **4**, and the fully condensed Schiff base, $(\mathrm{BZA})_2\mathrm{IPAH}$, **5**, could be isolated as crystalline solids.



(AEP)IPAH
4



$(\mathrm{BZA})_2\mathrm{IPAH}$
5

The electronic spectra of **4** and **5** exhibit solvent-dependent behavior similar to that previously reported for Schiff bases derived from salicylaldehyde.[19,20] For example, *N*-methylsalicylaldimine exhibits a strong absorption band at 31 700 cm^{-1} (4500 L mol^{-1} cm^{-1}) in solvents of low polarity, whereas in a polar solvent (e.g., absolute ethanol) this band is diminished in intensity and a new band appears at 25 000 cm^{-1} (~1000 L mol^{-1} cm^{-1}). This low-energy band is attributed to a keto amine tautometer in equilibrium with the familiar enol imine Schiff base formulation of salicylaldimines.[20] For **4** and **5** the corresponding bands for the two tautomers are shifted to lower energies owing to the more extensive conjugation existing in these compounds. In cyclohexane, the band observed near 28 300 cm^{-1} (Table II) for both compounds is attributed to the enol imine form. In solvents of higher dielectric constant a new band, attributed to the keto amine tautomer, develops at ~22 300 cm^{-1} coupled with a decrease in the intensity of the 28 300-cm^{-1} band. The stabilization of zwitterionic resonance forms of the keto amine form by the more polar solvents is an important aspect of the proposed tautomeric equilibrium. The hydrogen-bonding ability of

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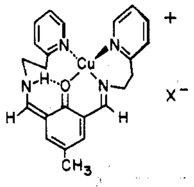
methanol probably accounts for the increase of the keto amine tautomer over that found in acetonitrile, despite the higher dielectric constant of the latter solvent. In a similar manner the increased tendency of **4** to form the keto amine tautomer as compared to **5** probably reflects the ability of the pyridine ring to provide stabilization of this form via internal hydrogen bonding.

The titration of **5** with $Cu(CH_3CN)_4^+$ in acetonitrile or methanol produces a decrease in the 28 400-cm^{-1} band and the appearance of a new band at 22 400 cm^{-1} which is essentially identical with the intense low-energy band of $Cu[(AEP)_2IPAH]^+$. Unfortunately, the interaction between Cu(I) and $(BZA)_2IPAH$ is not quantitative in acetonitrile and the stoichiometry of the complex could not be determined for the spectrophotometric titration. In methanol, both $Cu(CH_3CN)_4^+$ and the Cu(I) complex with $(BZA)_2IPAH$ disproportionate slowly over the course of the titration and quantitative data are again not possible. Despite these problems, the qualitative spectral changes which occur upon the interaction of Cu(I) with **5** indicate that the essential chromophore for the 22 600-cm^{-1} band of $[Cu(AEP)_2IPAH]^+$ involves the two imine functions and the phenolic group of the Schiff base ligand, **2**. No comparable spectral change was observed upon the addition of Cu(I) to solutions of the Schiff base derived from 2-(2-aminoethyl)pyridine and salicylaldehyde. We therefore suggest that the intense red color of $[Cu(AEP)_2IPAH]^+$ arises from a π–π* transition within a keto amine tautomer of the ligand induced and stabilized by coordination with Cu(I). The proposed structure of the complex, **6**, includes coordination by the two pyridine groups to yield a pseudotetrahedral structure which is shown to be quite favorable from molecular models. No direct evidence of pyridine coordination is available from infrared or optical spectroscopy, but the known tendency of Cu(I) to bind pyridine[21] and the enhanced stability of the Cu(I) complex with $(AEP)_2IPAH$ compared to that of the complexes with **4** or **5** strengthens this conclusion.



6a, $X = CuCl_2^-$
b, $X = BF_4^-$

The mononuclear complexes $[Cu^I(AEP)_2IPAH]BF_4$ and $[Cu^I(AEP)_2IPAH]Cu^ICl_2$ containing the protonated form of ligand **2** provide an interesting contrast to the pyrazolate-bridged binuclear Cu(I) complex **3** with deprotonated **2** reported elsewhere.[13] The failure of the deprotonated form of **2** to stabilize a binuclear Cu(I) species in the absence of a pyrazolate bridge emphasizes the major role of the pyrazolate anion in producing Cu(I)···Cu(I) complexes such as **3** which are stable toward disproportionation.

Knowledge of the nature of Cu(I) complexes formed by **2** in the absence of a pyrazolate bridge leads to possible interpretation of the irreversible electrochemical behavior observed for the binuclear Cu(II) complexes **1**. The hypothetical two-electron reduction

$$[(Cu_2(AEP)_2IPA)Cl]^+ + 2Cl^- + H^+ + 2e^- \rightarrow [Cu(AEP)_2IPAH]^+ + CuCl_2^- + Cl^-$$

requires removal of one copper ion from the ligand and its stabilization as $CuCl_2^-$ and protonation and tautomerization of the ligand in order to produce $[Cu(AEP)_2IPAH]^+$. These extensive rearrangements readily account for the highly irreversible electrochemistry of **1**. Chemical reduction of $[(Cu_2(AEP)_2IPA)Cl]Cl_2$ to $[Cu(AEP)_2IPAH]CuCl_2$ has been achieved. The reaction of a suspension of $[(Cu_2(AEP)_2IPA)Cl]Cl_2$ in acetonitrile with a small amount of a concentrated aqueous solution of sodium ascorbate generates a yellow-orange solution which exhibits an electronic spectrum close to that observed for $[Cu(AEP)_2IPAH]^+$ in acetonitrile. The solid complex $[Cu(AEP)_2IPAH]CuCl_2$ may be isolated from these solutions. In this chemical reduction the aqueous ascorbate solution acts as a proton source for the protonation of the ligand.

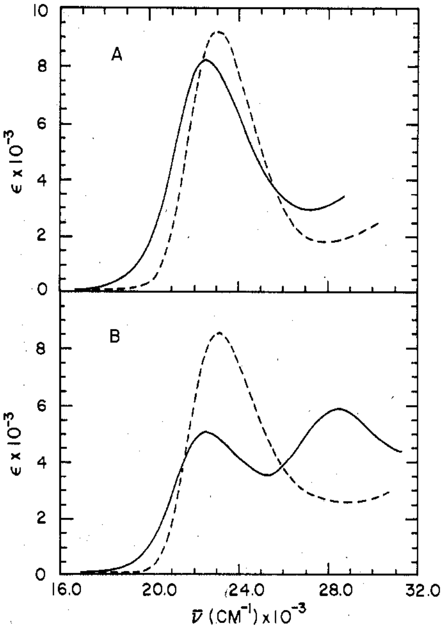


Figure 2. (A) Absorption spectra of $[Cu(AEP)_2IPAH]BF_4$ in Me_2SO under N_2 atmosphere (—) and under CO atmosphere (---). (B) Absorption spectra of $[Cu(AEP)_2IPAH]CuCl_2$ in acetonitrile under N_2 atmosphere (—) and under CO atmosphere (---).

Reaction with Oxygen. Oxidation of $[Cu(AEP)_2IPAH]CuCl_2$ in acetonitrile solution occurs rapidly upon exposure to air and produces a green crystalline complex formulated as $[(Cu_2(AEP)_2IPA)OH]Cl_2{\cdot}H_2O$.[22] The room-temperature magnetic moment of this complex (μ_B = 1.04 (25 °C)) is in close agreement with hydroxo-bridged binuclear species reported previously.[1,11,12] The hydroxo-bridged formulation is further supported by an infrared band at 3450 cm^{-1} characteristic of a bridging hydroxide.[1,11b] The O–H stretching frequency of the water of hydration is assigned to a band observed at 3340 cm^{-1}.[1] The remainder of the infrared spectrum of the oxidized product is essentially identical with that of other binuclear Cu(II) complexes of the deprotonated form of **2**.[1] The d → d spectrum of $[(Cu_2(AEP)_2IPA)OH]Cl_2{\cdot}H_2O$ contains a weak band at 13 700 cm^{-1} with a shoulder at 11 000 cm^{-1}. This type of spectrum has been observed by Robson for a binuclear complex with the two copper(II) ions in slightly different square-planar environments.[11b] The analogous oxidation of $[Cu(AEP)_2IPAH]BF_4$ generates no isolable solid. The complicated electronic spectra of oxidized solutions of the fluoroborate salt probably represent mixtures of binuclear complex, mononuclear complex, and free ligand.

Reaction with Carbon Monoxide. Red solutions of $[Cu(AEP)_2IPAH]^+$ in Me_2SO or acetonitrile are converted to yellow upon exposure to an atmosphere of carbon monoxide

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(22) Anal. Calcd for $C_{23}H_{26}N_4O_3Cl_2Cu_2$: C, 45.70; H, 4.34. Found: C, 45.82; H, 4.59.

at room temperature. This color change is attributed to the formation of a CO adduct of $[Cu(AEP)_2IPAH]^+$ which is characterized by an electronic absorption band at 23 000 cm^{-1} (ϵ = 9300 (Me_2SO), 7900 (acetonitrile)) (Figure 2). The presence of CO causes the disappearance of the absorption band for the free ligand (28 300 cm^{-1}) in acetonitrile solution, apparently favoring the formation of the intact complex as the CO adduct. Removal of CO by vacuum/N_2 cycles at 25 °C restores the system to essentially the initial equilibrium state as shown spectrophotometrically. Attempts to determine the stoichiometry of the adduct in Me_2SO by measuring the extent of adduct formation as a function of CO pressure were unsuccessful owing to the slow disproportionation of $[Cu(AEP)_2IPAH]^+$.

Solid carbon monoxide adducts of both salts of $[Cu(AEP)_2IPAH]^+$ were isolated by exposing a concentrated solution of the complex in acetonitrile to CO. These yellow crystalline adducts were stable only under a CO atmosphere and exhibited a slow loss of CO when stored under N_2. The infrared spectra of the two adducts reveal an intense band at 2075 cm^{-1} characteristic of a terminally bound CO molecule.[23] The remainder of the infrared spectra were essentially identical with those of the respective $[Cu(AEP)_2IPAH]^+$ salts.

The interaction of CO with Cu(I) complexes is well-known,[24] and among the copper(I) carbonyl species with nitrogen-donor ligands recently studied,[24-30] several have possessed sufficient stability to allow X-ray diffraction studies.[24-28] With one exception,[27] the structures of these carbonyl adducts show a pseudotetrahedral geometry about the Cu(I) with a terminally bonded CO. Gagnê and coworkers[27] have reported a unique five-coordinate Cu(I) complex with a planar N_4 macrocyclic ligand and an axially bonded CO. The Cu(I)–CO species exhibit values of ν_{CO} over the range 2055–2091 cm^{-1}. The reversibility of the CO adduct formation varies widely with the solid complexes $[Cu(dien)CO]BPh_4$[25,31] and $[Cu_2(hm)_3(CO)_2](BPh_4)_2$[26,31] stable toward loss of CO in vacuo and by heating. In solution, the copper(I)–histamine complexes are reversible CO carriers.[26] Varying degrees of instability toward loss of CO are exhibited by $[Cu(en)CO]Cl$,[29,31] $[Cu(HB(pz)_3)CO]$,[30,31] and the five-coordinate carbonyl adduct of the Cu(I) macrocycle.[27] Hemocyanin reversibly combines with CO and carboxyhemocyanin[32] exhibits ν_{CO} = 2063 cm^{-1}. In view of the crystallographic results for Cu(I)–CO complexes a probable structure for $[Cu(AEP)_2IPAH(CO)]^+$ would have a pseudotetrahedral stereochemistry with the CO adding to a three-coordinate Cu(I) center or displacing a weakly bound pyridine donor from the proposed structure **6**. A five-coordinate adduct seems less likely since the ligand $(AEP)_2IPAH$ does not constrain four-coordination upon the Cu(I) in the same manner as a macrocyclic ligand.

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Registry No. 4, 73940-71-3; **5**, 73940-72-4; **6a**, 73970-89-5; **6b**, 73970-88-4; $[Cu(AEP)_2IPAH(CO)]BF_4$, 73970-90-8; $[Cu(AEP)_2IPAH(CO)]CuCl_2$, 73953-28-3; IPAH, 7310-95-4; 2-(2-aminoethyl)pyridine, 2706-56-1; benzylamine, 100-46-9; $Cu(CH_3CN)_4BF_4$, 15418-29-8; $[(Cu_2(AEP)_2IPA)OH]Cl_2$, 73970-91-9.

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Kinetics Studies of Ligand Dissociation from Bis-Substituted Derivatives of Hexacarbonylchromium, *trans*-$Cr(CO)_4L_2$ (L = $P(C_4H_9)_3$, $P(OC_6H_5)_3$, $P(OCH_3)_3$, $P(C_6H_5)_3$, and $As(C_6H_5)_3$)

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The kinetics of ligand replacement on *trans*-$Cr(CO)_4L_2$ for L = $P(OC_6H_5)_3$, $P(C_4H_9)_3$, and $P(OCH_3)_3$ by CO have been studied between 100 and 140 °C in decane solution. The reactions proceed by rate-determining dissociation of the ligand L. Qualitative data are also reported for $Cr(CO)_4(P(C_6H_5)_3)_2$ and $Cr(CO)_4(As(C_6H_5)_3)_2$. The ordering of dissociation rates $As(C_6H_5)_3 > P(C_6H_5)_3 > P(C_4H_9)_3 > P(OC_6H_5)_3 > CO > P(OCH_3)_3$ is consistent with a very strong dependence of the π-bonding capability of the ligand, in contrast to dissociations from $Cr(CO)_5L$. Activation parameters are presented for dissociations of $P(OC_6H_5)_3$, $P(C_4H_9)_3$, and $P(OCH_3)_3$.

Introduction

Ligand dissociation to open a coordination site on an organometallic center is a very important step in reactions of organometallic compounds. Our recent study of dissociations of different ligands from $Cr(CO)_5L$ (L = $P(C_6H_5)_3$, $P(C_4H_9)_3$, $P(OC_6H_5)_3$, $P(OCH_3)_3$, and $As(C_6H_5)_3$) has shown the rates to be very dependent on the nature of the ligand dissociating; the range of dissociation rates spans five orders of magnitude.[1] The rates could not be correlated with steric size, σ-bonding ability or π-bonding ability; however, the strongly binding

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