value of K_3[Fe(ent)], 0.75, eluted on the same system.

Thin-layer chromatography of the $[Rh(ent)]^{3-}$ indicates that it is much more stable to air than the $[Cr(ent)]^{3-}$ complex. After 3 h of exposure at room temperature only one sharp spot is observed using the TLC procedure previously described. The vis–UV spectra also remain constant. At 0 °C, $[Rh(ent)]^{3-}$ can be stored for at least 1 week with no apparent change. The chromatographic behavior on silica gel TLC plates of $[Cr(ent)]^{3-}$, $[Rh(ent)]^{3-}$, and $[Fe(ent)]^{3-}$ are very similar. Since the ionic radius of Fe^{3+} (0.645 Å) lies between those of Cr^{3+} (0.615 Å) and Rh^{3+} (0.665 Å) and is within 0.03 Å of each and because the $[Cr(ent)]^{3-}$ and the $[Rh(ent)]^{3-}$ absolute configurations have been reliably assigned, the configuration of the $[Fe(ent)]^{3-}$ may be given as Δ-cis with a good degree of certainty. Thus, assignment of the absolute configuration of $[Fe(ent)]^{3-}$ is confirmed as opposite to that known for all other siderophores with the exception of the recently characterized rhodotorulic acid complex.[18]

In summary: (1) The enterobactin complexes of Rh(III), Cr(III), and Fe(III) are identical in structure and are formed by octahedral coordination of the catechol oxygen atoms. (2) There is one isomer which is preferred, the Δ absolute configuration, which is opposite in chirality to the ferrichromes and mycobactin.

Acknowledgment. Research support of the NIH from Grant No. AI 11744 and a postdoctoral fellowship to J.V.M. are gratefully acknowledged.

Registry No. $[Co(en)_3][Rh(cat)_3]$, 67577-16-6; $K_3[Rh(cat)_3]$, 67577-17-7; Δ-$K_3[Rh(cat)_3]$, 67597-64-2; Λ-$K_3[Rh(cat)_3]$, 67597-65-3; Δ-*cis*-K_3[Rh(ent)], 67577-18-8.

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Binuclear Metal Complexes. 1. Dicopper(II) Complexes with Binucleating Ligands Derived from 2-Hydroxy-5-methylisophthalaldehyde and 2-(2-Aminoethyl)pyridine or Histamine

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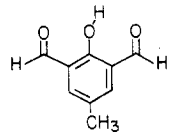
Dicopper(II) complexes are described with the binucleating Schiff-base ligands derived from the condensation of 2-hydroxy-5-methylisophthalaldehyde, **1**, and 2-(2-aminoethyl)pyridine or histamine and the corresponding secondary amine ligands produced by chemical reduction of the Schiff bases. Analytical data and conductance, spectral, and magnetic studies support the binuclear formulations **2–5** of these complexes. The antiferromagnetic interaction between the copper(II) ions is dependent on the bridging anion with values of $2J$ ranging from −385 to −545 cm^{-1} for the hydroxo-bridged species and from −156 to −230 cm^{-1} for the chloro-bridged species. Electrochemical reductions of the complexes are irreversible and ill-defined and do not lead to stable dicopper(I) complexes of the binucleating ligands. Reaction of the hydroxo-bridged binuclear copper(II) complexes with sodium ascorbate yields an ascorbate adduct characterized by intense charge-transfer bands.

Introduction

Interest in binuclear copper centers has focused primarily on the magnetic exchange (spin–spin) interaction between the two paramagnetic ($S = {}^1/_2$) cupric ions[1-3] as determined by bulk susceptibility or electron spin resonance (ESR) measurements. Since binuclear copper centers are proposed[4,5] to be part of the active site of several multicopper-containing proteins, the redox behavior of binuclear copper chelates assumes increased importance. Malmström[4] originally proposed that the type 3 (ESR nondetectable) copper in laccase consists of a pair of antiferromagnetically coupled Cu(II) ions which are capable of acting as a two-electron oxidant. More recently, Mason[5] has reviewed the evidence for binuclear copper centers in a variety of proteins. Since little information is known about the nature of these binuclear centers, it is appropriate to examine the properties of simple binuclear chelate systems in order to provide a basis for understanding the biological analogues.

Complexes with two metal ions in close proximity can result from the association of two monomeric units via an appropriate bridging group or from the incorporation of two metal ions into a single binucleating ligand. The latter route offers the advantage that the presence of the binuclear form in solution is not governed by a monomer ⇌ dimer equilibrium, and all of the complexes reported here are based on binucleating ligands. Robson[6] and Okawa and Kida[7] have introduced 2-hydroxy-5-methylisophthalaldehyde, **1**, as an important



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building block for binucleating macrocyclic and nonmacrocyclic ligands and have reported extensively on the

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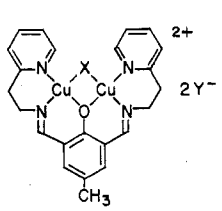
Table I. Analytical Data for the Copper Complexes Derived from 2-Hydroxy-5-methylisophthaladehyde

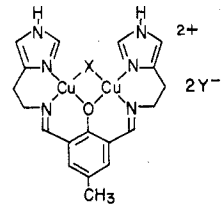
compd	%C		%H		%N		%Cl	
	calcd	found	calcd	found	calcd	found	calcd	found
$[(Cu_2(AEP)_2IPA)OH](ClO_4)_2$	38.66	38.60	3.39	3.30	7.84	7.71	9.92	9.72
$[(Cu_2(AEP)_2IPA)Cl]Cl_2$	45.67	45.42	3.83	3.87	9.26	9.06	17.58	17.58
$[(Cu_2(HA)_2IPA)OH](ClO_4)_2$	32.96	32.86	3.20	3.48	12.14	12.07	10.24	10.34
$[(Cu_2(HA)_2IPA)Cl]Cl_2 \cdot H_2O$	37.98	38.08	3.85	3.75	13.99	14.12	17.70	17.77
$[(Cu_2(H_2AEP)_2IPA)OH](ClO_4)_2$	38.45	38.54	3.94	3.99	7.79	7.56	9.87	9.81
$[(Cu_2(H_2HA)_2IPA)OH](ClO_4)_2 \cdot H_2O$	31.94	31.89	3.96	3.79	11.76	11.66	9.92	9.99

spectral and magnetic properties of transition-metal complexes with these types of ligands.[6,7]

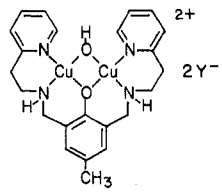
In this paper we report the synthesis and characterization of the dicopper complexes **2–5** of four new ligands based on



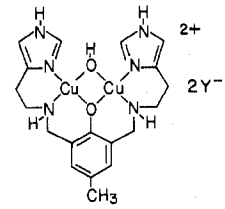
2a, X = OH, Y = ClO_4^-
2b, X = Y = Cl^-



3a, X = OH^-, Y = ClO_4^-
3b, X = Y = Cl^-



4, Y = ClO_4^-



5, Y = ClO_4^-

2-hydroxy-5-methylisophthalaldehyde. The ligands were designed in an attempt to provide soluble complexes containing heterocyclic amine donors which may promote stabilization of the Cu(I) oxidation state.

Experimental Section

Materials. The dialdehyde 2-hydroxy-5-methylisophthalaldehyde was prepared by the method of Ullman and Brittner.[8] Histamine (free base) was isolated from histamine dihydrochloride (Aldrich Chemical Co.) by the method of Pliml and Proteva.[9] Sodium ascorbate was prepared by reacting ascorbic acid (Merck and Co., Inc.) with sodium bicarbonate in water and precipitating the sodium ascorbate by the addition of 2-propanol. All other starting materials were reagent grade or better and were used as received.

Copper Complexes. μ-Hydroxo-μ-[2,6-bis[*N*-(2′-pyridylethyl)-iminomethyl]-4-methylphenolato]-dicopper(II) Perchlorate, 2a, $[(Cu_2(AEP)_2IPA)OH](ClO_4)_2$. A solution of 2-hydroxy-5-methylisophthalaldehyde (IPAH) (0.41 g, 2.5 mmol) in warm ethanol (25 mL) was reacted with 2-(2-aminoethyl)pyridine (AEP) (0.61 g, 5.0 mmol). The resulting solution was stirred for 15 min and an aqueous solution (10 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.85 g, 5 mmol) was added with stirring. A blue crystalline solid precipitated from the dark green solution. The complex was recrystallized ($EtOH/H_2O$ (25/75)), filtered, washed with water, and dried under vacuum at 78 °C; mp 268–270 °C (dec).

μ-Chloro-μ-[2,6-bis[*N*-(2′-pyridylethyl)iminomethyl]-4-methylphenolato]-dicopper(II) Chloride, 2b, $[(Cu_2(AEP)_2IPA)Cl]Cl_2$. IPAH (0.41 g, 2.5 mmol) in warm ethanol was reacted with AEP (0.61 g, 5.0 mmol). An ethanolic solution of $CuCl_2 \cdot 2H_2O$ (0.85 g, 5.0 mmol) was added to the orange ligand solution. The reaction mixture was reduced in volume on a rotary evaporator yielding a brown microcrystalline solid. This solid was collected, recrystallized from methanol, and vacuum-dried at 78 °C; mp 245–250 °C (dec).

μ-Hydroxo-μ-[2,6-bis[*N*-(4′-imidazolylethyl)iminomethyl]-4-methylphenolato]-dicopper(II) Perchlorate, 3a, $[(Cu_2(HA)_2IPA)OH](ClO_4)_2$. IPAH (0.41 g, 2.5 mmol) was dissolved in warm ethanol and reacted with histamine (free base) (0.55 g, 5.0 mmol) in 10 mL of water. $Cu(ClO_4)_2 \cdot 6H_2O$ (1.85 g, 5.0 mmol) in aqueous solution was added to the ligand solution with stirring. Upon standing, a crystalline solid formed, which was filtered, recrystallized from water, and vacuum-dried at 78 °C; mp >270 °C.

μ-Chloro-μ-[2,6-bis[*N*-(4′-imidazolylethyl)iminomethyl]-4-methylphenolato]-dicopper(II) Chloride, 3b, $[(Cu_2(HA)_2IPA)Cl]Cl_2$. Histamine dihydrochloride (0.92 g, 5.0 mmol) was dissolved in 100 mL of a 0.1 N sodium hydroxide solution and reacted with a warm ethanolic solution of IPAH (0.41 g, 5.0 mmol). The resulting ligand solution was reacted with an aqueous solution of $CuCl_2 \cdot 2H_2O$ (0.85 g, 5.0 mmol) and evaporated until crystals began to form. Cooling yielded a green crystalline product which was collected, recrystallized from methanol, and vacuum-dried at 78 °C. The complex was slightly hygroscopic; mp 245–248 °C (dec).

μ-Hydroxo-μ-[2,6-bis[*N*-(2′-pyridylethyl)aminomethyl]-4-methylphenolato]-dicopper(II) Perchlorate, 4, $[(Cu_2(H_2AEP)_2IPA)OH](ClO_4)_2$. An ethanolic solution (25 mL) of IPAH (0.41 g, 2.5 mmol) was reacted with AEP (0.61 g, 5.0 mmol). This solution was treated with 0.5 g of sodium borohydride in an ethanol–water mixture (50/50; 25 mL). After 1 h, the reaction was neutralized with dilute perchloric acid and filtered. The filtrate was reacted with 1.85 g of $Cu(ClO_4)_2 \cdot 6H_2O$ (5.0 mmol) in water (15 mL). The resulting green solution was evaporated on a rotary evaporator to 30 mL and cooled. The green solid which formed was isolated by filtration and recrystallized from a concentrated aqueous solution of sodium perchlorate. The green crystalline solid was filtered, washed with a small amount of cold water, and vacuum-dried at 78 °C. The hygroscopic complex was stored in a desiccator; mp 232–235 °C (dec).

μ-Hydroxo-μ-[2,6-bis[*N*-(4′-imidazolylethyl)aminomethyl]-4-methylphenolato]-dicopper(II) Perchlorate, 5, $[(Cu_2(H_2HA)_2IPA)OH](ClO_4)_2 \cdot H_2O$. A solution of IPAH (0.41 g, 2.5 mmol) in warm ethanol (25 mL) was reacted with an aqueous solution (10 mL) of histamine (0.55 g, 5.0 mmol). This ligand solution was reacted with an ethanol–water (50/50; 20 mL) solution of sodium borohydride (0.5 g). After 1 h, the reaction was quenched and neutralized with a dilute perchloric acid solution. An aqueous solution (10 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.85 g, 5.0 mmol) was added and the reaction mixture was cooled overnight. The green needle crystals were collected, recrystallized from water, and dried under vacuum at 78 °C. The hygroscopic complex was stored in a desiccator; mp >270 °C.

Physical Measurements. Elemental analyses (Table I) were provided by Galbraith Laboratories, Inc., Knoxville, Tenn. **Infrared spectra** were measured on either a Beckman IR-8 or IR-10 spectrophotometer with Nujol mulls or KBr pellets. The spectra were calibrated with the 2851- and 1601-cm^{-1} absorption bands of polystyrene. **Electronic absorption spectra** were obtained with a Cary Model 14 spectrophotometer. **Magnetic susceptibilities** at room temperature were determined by the Faraday method using a Varian V-4004 electromagnet and a Cahn RG electrobalance. $Hg[Co(NCS)_4]$ was used as a standard and diamagnetic corrections were calculated from a table of Pascal's constants.[10] Variable-temperature magnetic data were obtained at the University of North Carolina with instrumentation described previously.[11] **Conductivity measurements** were obtained using a Beckman RC-19 conductivity bridge. Triply distilled water or spectrophotometric grade methanol was used as solvent. **Cyclic voltammetry** and **controlled-potential electrolyses** were carried out with electrochemical equipment consisting of a Princeton Applied Research Model 373 potentiostat, a Wavetek Model 133 function generator, and a Houston Model 2000 XY recorder. The electrochemical cells employed were constructed according to accepted concepts in cell design.[12,13] Platinum electrodes were cleaned by treatment with nitric acid followed by a thorough rinsing with distilled water and drying. All electrochemical measurements were made relative to saturated

Table II. Electronic Spectra of the Binuclear Copper(II) Complexes

complex	solvent	ν_{max}, cm^{-1} (ϵ)
$[(Cu_2(AEP)_2IPA)OH](ClO_4)_2$	H_2O	16 000 (100), 26 300 (sh), 27 400 (6900)
	MeOH	16 300 (135), 26 000 (sh), 27 500 (8300)
$[(Cu_2(AEP)_2IPA)Cl]Cl_2$	H_2O	16 000 (90), 26 300 (sh), 27 500 (7400)
	MeOH	13 900 (175), 20 800 (sh), 26 700 (7000)
$[(Cu_2(HA)_2IPA)OH](ClO_4)_2$	H_2O	16 400 (90), 26 300 (sh), 27 800 (6900)
	MeOH	16 400 (126), 26 000 (sh), 27 500 (6800)
$[(Cu_2(HA)_2IPA)Cl]Cl_2 \cdot H_2O$	H_2O	16 300 (83), 26 700 (sh), 27 500 (6100)
	MeOH	14 100 (155), 27 000 (7350), 27 800 (sh)
$[(Cu_2(H_2AEP)_2IPA)OH](ClO_4)_2$	H_2O	16 400 (130), 29 400 (2300), 34 500 (sh)
	MeOH	16 500 (185), 26 900 (2600)
$[(Cu_2(H_2HA)_2IPA)OH](ClO_4)_2 \cdot H_2O$	H_2O	16 500 (120), 30 100 (2000), 34 700 (3800)
	MeOH	16 500 (164), 28 300 (2100)

calomel electrodes constructed according to published design specifications.[13]

Results and Discussion

Synthesis of the Complexes. Analytical data (Table I) indicate that the desired stoichiometries have been achieved for both the Schiff base (**2**, **3**) and reduced Schiff base (**4**, **5**) dicopper complexes. The complexes of **2** and **3** containing either chloride or hydroxide bridging groups were isolated as crystalline solids from the reaction of appropriate cupric salts with the Schiff-base ligands generated in situ. Complexes **4** and **5** were prepared as hydroxo-bridged species by the reduction of the Schiff-base ligands with sodium borohydride prior to reaction with copper(II). All attempts to isolate the free Schiff-base ligands resulted in the formation of orange oils which were not characterized. No attempts were made to isolate the reduced ligands.

Infrared Spectra. The presence or absence of certain bands in the generally complicated infrared spectra may be utilized to establish the nature of the complexes. The absence of the dialdehyde carbonyl stretching frequency (1675 cm^{-1}) in all of the complexes indicates the complete formation of azomethine (C=N) linkages. The C=N stretching frequency occurs in the range 1630–1640 cm^{-1} for all of the Schiff base metal complexes in agreement with the assignment of Okawa and Kida[7f] for a similar series of compounds. Complexes in which the azomethine linkages have been reduced lack the strong C=N stretching band but exhibit a moderate intensity band at 1625 cm^{-1} attributable to an aromatic stretching mode. The azomethine reduction is further confirmed by the appearance of a secondary amine N–H stretching band in the region 3230–3250 cm^{-1}. The hydroxo-bridged complexes exhibit a sharp band in the region 3480–3600 cm^{-1} which is assigned to the bridging O–H stretch on the basis of previous observations.[6g] The bridging O–H stretching band is readily distinguished from the O–H stretching bands for waters of hydration which occur at 3200–3300 cm^{-1}. All of the perchlorate salts show strong bands near 1100 cm^{-1} (antisymmetric stretch) and sharp bands at 620–625 cm^{-1} (antisymmetric bend), indicative of uncoordinated perchlorate anions.[14]

Electronic Spectra and Conductance Measurements. All of the hydroxo-bridged species exhibit broad d → d absorption bands (Table II) at (16.0–16.5) × 10^3 cm^{-1} (ϵ = 80–130 based on $[(Cu_2L)OH]^{2+}$ units) indicative of either a square-planar Cu(II) environment or a distorted octahedral system with weak apical coordination of solvent molecules. The position of the d → d transition does not vary significantly in water vs. methanol solutions for the hydroxo-bridged complexes. The energies of these d → d transitions compare favorably with similar mononuclear[15,16] and binuclear[6g] copper(II) chelates with N_2O_2 coordination environments.

The proposed structures for the hydroxo-bridged complexes are further supported by molar conductance values which show them to be 2:1 electrolytes in both aqueous and methanol solutions. Plots of molar conductance vs. $C^{1/2}$ were linear within the range 10^{-3}–10^{-4} M, and treatment of these data by a graphical procedure[17] to determine electrolyte type confirmed the 2:1 behavior.

Table III. Concentration Dependence of the Conductance and Spectra of the Chloro-Bridged Complexes in Methanol

complex	10^4 × concn, M	Λ_m[a]	ν_{max}[b] (ϵ)
$[(Cu_2(AEP)_2IPA)Cl]Cl_2$	10	145	13.9 (184)
	2	248	14.8 (145)
	1	288	15.6 (112)
$[(Cu_2(HA)_2IPA)Cl]Cl_2 \cdot H_2O$	10	155	14.1 (154)
	2	202	14.4 (140)
	1	221	14.9 (112)

[a] Molar conductivity (Ω^{-1} cm^{-1} mol^{-1}) at 25 °C. [b] In cm^{-1} × 10^3.

The spectra of the chloro-bridged complexes are solvent dependent and exhibit grossly different behavior in water and methanol. In nonaqueous solvents (e.g., methanol and acetonitrile) the d → d bands of the chloro-bridged complexes occur at (13.9–14.1) × 10^3 cm^{-1} (1 × 10^{-3} M solutions). This band shift to lower energies compared to that for the hydroxo-bridged species is due to the combined effects of a N_2OCl coordination environment and some degree of apical coordination of chloride ions to give a five-coordinate geometry. At concentrations greater than 1 × 10^{-3} M in methanol, the chloro-bridged complexes behave as less than 2:1 electrolytes, indicating partial coordination of the chloride counterions. Apical coordination of chloride ions to produce square-pyramidal Cu(II) has been observed for similar compounds in the solid state by Robson and co-workers.[6i]

In aqueous solution the d → d transitions of the chloro-bridged species are identical within experimental error to those observed for the hydroxo-bridged complexes with the same ligands. This behavior is attributed to a hydrolytic process whereby the chloride bridge is exchanged for a hydroxide bridge in water. Similar behavior has been observed previously[6g] for complexes of this type and conductance data are in agreement with the hydrolytic behavior.

Freshly prepared solutions (ca. 10^{-3} M) of the chloro-bridged complexes in water yield conductance values greater than 2:1 electrolytes. Upon dilution the molar conductivities rise sharply and reach values of 450–475 Ω^{-1} cm^{-2} mol^{-1} at 10^{-4} M. This phenomenon is attributed to the hydrolytic process whereby the formation of a hydroxo-bridged species is coupled to the liberation of a highly conducting proton:

$$[(Cu_2(AEP)_2IPA)Cl]^{2+} + 2Cl^- + H_2O \rightleftarrows [(Cu_2(AEP)_2IPA)OH]^{2+} + 3Cl^- + H^+$$

In methanol, the molar conductivities of the chloro-bridged species (Table III) also increase with dilution beyond that expected for a 2:1 electrolyte but the effect is not as dramatic as for aqueous solutions. The positions and intensities for the d → d transitions (Table III) of the chloro-bridged complexes exhibit a shift toward that of a hydroxo (methoxo)-bridged

Table IV. Magnetic Data for the Binuclear Cu(II) Complexes

complex	μ_{eff}, μ_B (T, K)	g	$-2J$, cm^{-1}
$[(Cu_2(AEP)_2IPA)OH](ClO_4)_2$	1.02 (296)	2.03	385
$[(Cu_2(H_2AEP)_2IPA)OH](ClO_4)_2$	1.01 (296)	2.29	439
$[(Cu_2(HA)_2IPA)OH](ClO_4)_2$	0.99 (295)	2.15	529
$[(Cu_2(H_2HA)_2IPA)OH](ClO_4)_2 \cdot H_2O$	0.94 (296)	2.17	545
$[(Cu_2(HA)_2IPA)Cl]Cl_2 \cdot H_2O$	1.61 (295)	2.17	156
$[(Cu_2(AEP)_2IPA)Cl]Cl_2$	1.54 (296)	2.14	230

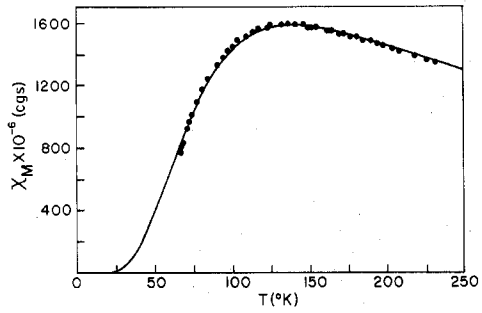


Figure 1. Temperature-dependent magnetic susceptibility of $[(Cu_2(HA)_2IPA)Cl]Cl_2 \cdot H_2O$.

species upon dilution in methanol. An interpretation of these spectral changes is complicated by the fact that apical coordination by Cl^- is lost upon dilution as well as the exchange of the bridging group.

All of the Cu(II) complexes of the Schiff-base ligands exhibit an intense band in the range (26.3–27.8) $\times 10^3$ cm^{-1} (Table II). The major component of these bands is assigned as a $\pi \rightarrow \pi^*$ transition involving delocalization throughout the azomethine chromophores. The shoulders evident in all of these bands may represent a splitting of the $\pi \rightarrow \pi^*$ band[16] or the presence of another electronic transition. Waters and Wright[18] have assigned the 27.0 $\times 10^3$ cm^{-1} band in salicylaldimine copper(II) complexes as a $\pi \rightarrow \pi^*$ transition and speculated that the shoulder at 25.0 $\times 10^3$ cm^{-1} represents a $d \rightarrow \pi^*$ charge-transfer transition. In any event, the major portion of the 27.0 $\times 10^3$ cm^{-1} band in the present complexes is lost upon the saturation of the azomethine bonds and its origin must be in these chromophoric groups.

Magnetic Studies. The room-temperature magnetic moments of the hydroxo-bridged complexes range from 0.9 to 1.1 μ_B (Table IV). These values are far below both the calculated spin-only value of 1.73 μ_B for Cu(II) and the experimentally determined moments of magnetically discrete Cu(II) complexes (1.8–2.0 μ_B)[19] and indicate a high degree of antiferromagnetic interaction between the metal centers. The chloro-bridged species show a lesser degree of spin–spin coupling, possessing room-temperature magnetic moments of 1.50–1.65 μ_B. The χ_m vs. T dependence for the hydroxo-bridged species exhibits a smooth curve which never passes through a maximum in the region studied. In contrast, the curves obtained for the chloro-bridged species (Figure 1) reach a maximum at approximately 125 K before decreasing to zero. Analysis of the χ_m vs. T curves was carried out by fitting the data to the Bleaney–Bowers equation[20] for simple Cu(II)

$$\chi_m = \frac{Ng^2B}{3kT}\left[1 + \tfrac{1}{3}\exp\left(-\frac{2J}{kT}\right)\right]^{-1}$$

dimers, where $2J$ is the energy difference between the singlet and triplet states and where χ_m is the molar susceptibility per metal ion. This procedure treats the complexes as a ground-state singlet with a low-lying triplet state. A simplex curve-fitting routine[21] was used to determine the parameters g and $2J$ for each set of magnetic susceptibility data. Figure 1 illustrates the type of "best fits" obtained. The $2J$ values which were determined range from −385 to −545 cm^{-1} for the hydroxo-bridged species and from −150 to −230 cm^{-1} for the chloro-bridged species (Table IV). These values are comparable to those obtained by Robson[6b,g] and Okawa and Kida[7b,d,f] for similar systems.

Table V. Spectral Data for the Reaction of the Binuclear Cu(II) Complexes with Sodium Ascorbate in Water (Room Temperature)

complex	ν_{max}, cm^{-1} (ϵ)[a]
$[(Cu_2(AEP)_2IPA)OH](ClO_4)_2$	15 600 (sh), 19 600 (2300)
$[(Cu_2(H_2AEP)_2IPA)OH](ClO_4)_2$	15 900 (sh), 22 700 (3400), 29 400 (2300)
$[(Cu_2(HA)_2IPA)OH](ClO_4)_2$	16 400 (sh), 20 000 (460)
$[(Cu_2(H_2HA)_2IPA)OH](ClO_4)_2 \cdot H_2O$	16 700 (sh), 24 400 (1900), 30 100 (sh)

[a] Measured with solutions containing >200:1 ascorbate:Cu_2L where constant values of ϵ are achieved.

The antiferromagnetic behavior of the binuclear complexes is attributed to spin–spin interactions occurring via a superexchange pathway rather than a direct metal–metal interaction. The Cu–Cu distance in our binuclear systems is estimated to be ~3.2 Å, based on the Cu–Cu distances of similar complexes[6g] for which structural data is available. This separation generally rules out any significant amount of direct Cu–Cu interaction. The large effect of the nature of the bridging moiety on the paramagnetism of the complex substantiates this superexchange mechanism. The observation that hydroxo bridges provide more effective pathways for spin–spin interactions than the chloro bridges has been well characterized in the dimeric Cu(II) systems studied primarily by Hatfield[1] and Hodgson.[2]

Electrochemistry. Electrochemical investigations of the complexes revealed no evidence for the formation of either a stable mixed-valence ($Cu^{II}Cu^{I}$) or binuclear Cu(I) complex upon reduction. The observed cyclic voltammetry behavior in acetonitrile is characterized generally by irreversible reductions directly to metallic Cu or to unstable Cu(I) species which rapidly disproportionate. The reduction of the hydroxo-bridged species occurs at −0.60 to −0.70 V vs. SCE and that of the chloro-bridged species at −0.20 to −0.25 V vs. SCE. $[(Cu_2(AEP)_2IPA)Cl]Cl_2$ was noted to undergo irreversible reduction without generating a Cu mirror on the electrode and was investigated further. Controlled-potential electrolysis of $[(Cu_2(AEP)_2IPA)Cl]Cl_2$ in acetonitrile at −0.4 V vs. SCE (n = 2.0 ± 0.2) yields an orange-red solution which is stable to disproportionation but is very sensitive to oxygen. A comparison of the spectrum of the electrogenerated species with that of a chemically synthesized monocopper(I) complex[22] of $(AEP)_2IPAH$ reveals that electrolysis has not produced a dicopper(I) complex of the binucleating ligand. A portion of the copper(I) produced upon reduction is present as a monocopper(I) complex with $(AEP)_2IPAH$ and the remainder is stabilized by coordination with acetonitrile or chloride ion (as $CuCl_2^-$). This observation illustrates the need for spectral verification of the production of intact Cu(I) complexes by electrochemical reduction in solvents such as acetonitrile or dimethyl sulfoxide where dissociated Cu(I) will be stabilized against disproportionation by coordination with the solvent. Appropriate n values and the absence of disproportionation are not sufficient evidence for the generation of a copper(I) complex.

Reaction of the Hydroxo-Bridged Complexes with Ascorbate. In view of the failure to produce stable low-valent species by electrochemical methods, attempts were made to chemically reduce the binuclear complexes. Dithionite, powdered zinc, or hydroquinone gave no reaction with the hydroxo-bridged Cu(II) complexes. The reaction of sodium ascorbate with $[(Cu_2(AEP)_2IPA)OH]^{2+}$ in deaerated aqueous solution produces a new electronic transition at 19.6 $\times 10^3$ cm^{-1} which

gives the solution an intense purple color. Similar spectral changes occur with the other hydroxo-bridged species (Table V) upon reaction with ascorbate ion. Spectral studies reveal that this is not a quantitative reaction but is governed by an equilibrium between the ascorbate ion and $[(Cu_2(AEP)_2IPA)OH]^{2+}$. Large excesses of ascorbate (50:1) are necessary to drive the reaction to near completion. The spectral changes are also reversibly temperature dependent with the intensity of the 19.6×10^3 cm^{-1} band dropping by one-third upon warming the solution from 15 to 50 °C. From these observations we conclude that the binuclear Cu(II) complex is not being reduced by the ascorbate to a mixed-valent or a Cu(I) state. We propose that the ascorbate ion forms a weak adduct with the binuclear copper complex and the intense color arises from a charge-transfer transition from the reducing ligand to the copper ion. The observed equilibrium in our view represents the formation of the adduct $[(Cu_2L)OH]^{2+}\cdot(ascorbate)^-$, where L represents a binucleating ligand, rather than a redox equilibrium producing an oxidized form of ascorbate and a reduced form of the complex. A rough approximation of the redox potentials of the reactants supports this explanation. The dehydroascorbic acid/ascorbate couple ($E_0' = 0.06$ V vs. NHE, water, pH 7)[23] should not be sufficient to reduce the hydroxo-bridged binuclear complexes considering the potentials obtained from the electrochemical studies. Furthermore a one-electron reduction producing a mixed-valence copper dimer and an ascorbate radical is ruled out since no ESR signals were observed for the ascorbate–binuclear complex solutions. Any redox reaction involving ascorbate radical formation would not be expected to be reversible since disproportionation of the radical would be rapid.

If excess sodium ascorbate is added to an air-saturated solution of $[(Cu_2(AEP)_2IPA)OH]^{2+}$, the intense purple color develops instantly and then slowly fades as the ascorbate is oxidized. Qualitative studies of O_2 uptake reveal that the ascorbate oxidation is catalyzed by the binuclear chelates but not nearly as effectively as by Cu^{2+} ion.[24] The chloro-bridged binuclear complexes are more easily reduced and the reaction of ascorbate with $[(Cu_2(AEP)_2IPA)Cl]^{2+}$ leads to a unique monocopper(I) complex with the binucleating ligand. This complex will be discussed in a subsequent paper.[22]

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Registry No. **2a**, 67328-74-9; **2b**, 67328-75-0; **3a**, 67328-77-2; **3b**, 67328-78-3; **4**, 67328-80-7; $[(Cu_2(H_2HA)_2IPA)OH](ClO_4)_2$, 67328-82-9; IPAH, 7310-95-4; AEP, 2706-56-1; histamine, 51-45-6; histamine dihydrochloride, 64068-30-0; sodium ascorbate, 134-03-2.

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