This conclusion is also a natural consequence of the extensive mixing of the $^2B_1$ ground state with the low-lying $^2B_1$ MLCT state ($Ru(db_1) \rightarrow sq(3b_1)$, vide supra) whose equilibrium configuration is $Ru^{III}(cat)(3b_1)^2$.

In contrast, the calculated Ru → q transition energies are significantly less than those observed, the difference being larger in the TClQ complex. The observed energies are also higher than the Ru → sq energy. The bands are also very broad, with half-bandwidths of 1990 and 1420 $cm^{-1}$ for the TClQ and DTBQ complexes, respectively, indicating that the excited state is highly distorted;[40] i.e., the reorganization energy is large and is consistent with the resonance Raman data cited above. The unexpected result that the MLCT transition to the quinone lies at a higher energy than that to the semiquinone, when the former is the better acceptor, is thus related to the much greater inner reorganization energy contribution to the former transition. Thus the extent of mixing of ground and excited states is much less in the quinone complexes than in the semiquinones.

The quinone acceptor orbital is mainly C=O $\pi^*$ in nature.[6] The electron-withdrawing nature of the Cl substituents in TClQ will increse the C=O bond order relative to DTBQ and thus increase the reorganizational energy. This may explain the increase in transition energy and bandwidth from DTBQ to TClQ.

The $3b_1(cat) \rightarrow (bpy)\pi^*(1)$ transition in the cat derivatives is also broad and has an observed energy greater than the calculated energy, indicative of a significant contribution from reorganization energy. The catecholate derivatives must therefore also have a relatively pure ground-state configuration, as expected in the absence of any low-lying CT states to mix into the ground state.

**Conclusions.** Assuming that these complexes contain ruthenium(II), there is essential agreement between the observed electronic spectra both as a function of oxidation state and dioxolene ligand substituent and the predictions based on the electrochemical potentials and the GF analysis.[6] Combined analysis involving both electrochemistry and optical spectroscopy provides a more complete understanding of the nature of the ground and excited states in these molecules. This is the most detailed assignment of dioxolene complexes that has yet been attempted. Low-temperature (liquid He) data should provide further data concerning the electronic structure of this interesting series of complexes, and such an investigation, in concert with ESR studies, is in hand.

**Acknowledgment.** The authors are indebted to the Natural Sciences and Engineering Council (Ottawa) and the Office of Naval Research (Washington, DC) for financial support. We also thank Prof. Milan Melnik, Dr. W. A. Nevin, and W. Liu for technical assistance.

**Registry No.** $Ru(bpy)_2(DTBCat)$, 99687-84-0; $Ru(bpy)_2(Cat)$, 99687-85-1; $Ru(bpy)_2(TClCat)$, 99687-86-2; $Ru(py)_4(DTBCat)$, 99687-87-3; $Ru(py)_4(TClCat)$, 99687-88-4; $[Ru(bpy)_2(DTBCat)]^+$, 99687-89-5; $[Ru(bpy)_2(Cat)]^+$, 99687-90-8; $[Ru(bpy)_2(TClCat)]^+$, 99687-91-9; $[Ru(py)_4(DTBCat)]^+$, 99748-27-3; $[Ru(bpy)_2(DTBQ)]^{2+}$, 99705-94-9; $[Ru(bpy)_2(Q)]^{2+}$, 99687-92-0; $[Ru(bpy)_2(TClQ)]^{2+}$, 99687-93-1; $[Ru(py)_4(DTBQ)]^{2+}$, 99687-94-2; $[Ru(py)_4(TClQ)]^{2+}$, 99687-95-3; $[Ru(py)_4(TClSq)]^+$, 99687-96-4; $[Ru(bpy)_2(DTBCat)]^{2-}$, 99687-97-5; $[Ru(bpy)_2(Cat)]^{2-}$, 99687-98-6; $[Ru(bpy)_2(TClCat)]^{4-}$, 99687-99-7; *cis*-$Ru(bpy)_2Cl_2$, 19542-80-4; $Ru(py)_4Cl_2$, 16997-43-6.

**Supplementary Material Available:** Table V, FTIR data (2 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie des Métaux de Transition et de Catalyse, UA au CNRS No. 424, Institut Le Bel, Université Louis Pasteur, 67070 Strasbourg Cedex, France, and UA au CNRS No. 405, Ecole Nationale Supérieure de Chimie de Strasbourg, 67008 Strasbourg, France

# Copper Complexes of a Flexible Binucleating Ligand. Syntheses and Spectroscopic, Thermodynamic, and Kinetic Studies

Marie-Thérèse Youinou,† John A. Osborn,*† Jean-Paul Collin,‡ and Philippe Lagrange‡

*Received July 16, 1985*

The synthesis of the macrocyclic "earmuff" ligand 1,4-bis((1-oxa-4,10-dithia-7-azacyclododec-7-yl)methyl)benzene, L, and its mononucleating analogue L′ is reported. L and L′ react with copper(I) to form the dinuclear and mononuclear complexes $[Cu_2L]X_2$, $[Cu_2L'_3]X_2$, and $[CuL']X$ (X = $BF_4$, $ClO_4$, $PF_6$, OTf). Binding of the donor groups has been investigated by NMR spectroscopy in a donor solvent (acetonitrile, dimethyl sulfoxide). The accessibility of the copper(II) centers to reaction is demonstrated by the formation of a stable bis(triphenylphosphine) adduct $[Cu_2L(PPh_3)_2]X_2$ as well as the reversible addition of carbon monoxide in propylene carbonate to $[Cu_2L]X_2$. The synthesis of the binuclear copper(II) complexes $[Cu_2L]X_4$ and $[Cu_2(\mu\text{-}OH)L]X_3$ and of the mononuclear species $[CuL']X_2$ as well as their characterization by spectroscopic methods is also reported. Finally the complexation of Cu(II) by L and L′ has been investigated by potentiometric and spectrophotometric means. Our results show the very high stability in water of $[Cu_2(\mu\text{-}OH)L]^{3+}$, which can be rapidly protonated under the appropriate conditions to form $[Cu_2L]^{4+}$, thereby demonstrating the conformational flexibility of L.

## Introduction

Binuclear copper complexes in which the two copper sites are in close proximity are of considerable interest. Much of this interest stems from the proposed existence of such bimetallic sites in several copper enzymes, particularly those concerned with oxygen transport, storage, and reactivity, e.g. hemocyanin and tyrosinase. The detailed mechanism of action of such sites of this type on model systems may help cast light on the nature of the interactions involved between the binuclear site, oxygen, and substrate. In the construction of such a model, an evident paradox presents itself. The less that is known of the structure and action of the enzyme, the more useful the model but the more difficult its construction. However, as the details of the natural structure become better defined, the model is easier to construct yet, in part, loses progressively its raison d'être.

When this work was started several years ago, little was known about the ligand environment about the two copper centers in hemocyanin. On the basis of UV/visible spectroscopy, imidazole[1] and sulfhydryl[2] groups were suggested as possible ligands. In the

† Université Louis Pasteur.
‡ Ecole Nationale Supérieure de Chimie de Strasbourg.

(1) (a) Lontie, R. *Clin. Chim. Acta* **1958**, *3*, 68. (b) Salvato, B.; Girhetti-Magaldi, A.; Ghiretti, F. *Biochemistry* **1974**, *13*, 4778.
(2) Amundsen, A. R.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6730.

0020-1669/86/1325-0453$01.50/0 © 1986 American Chemical Society

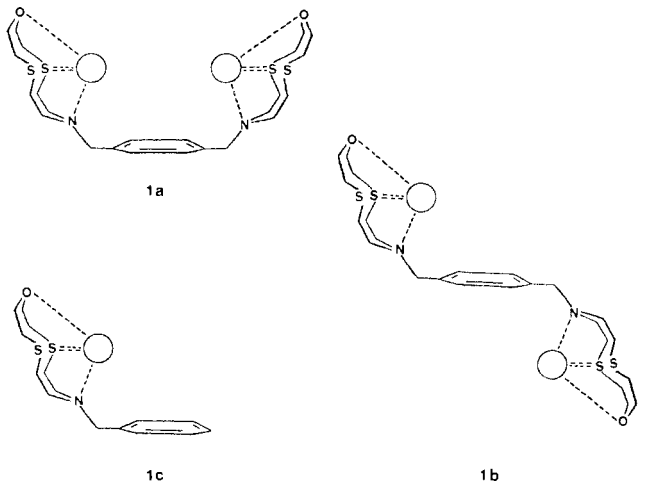


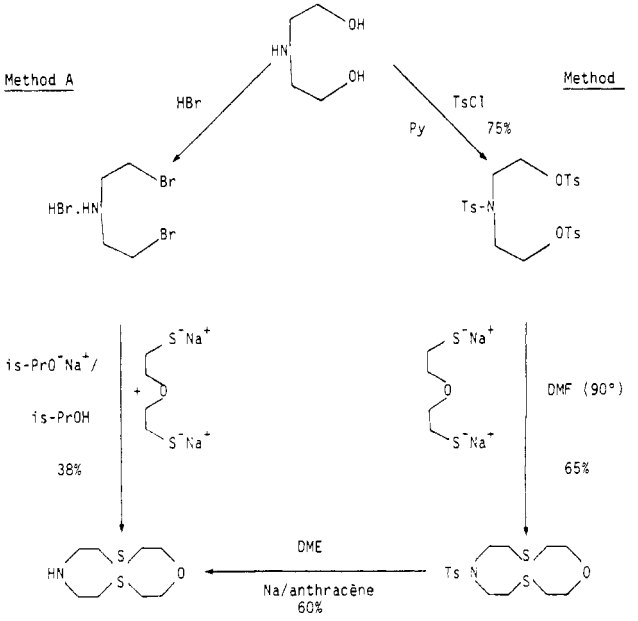

**Figure 1.** Representations of complexes of L in the "earmuff" configuration (**1a**), L in the "open" configuration (**1b**), and L′ (**1c**).

oxygenated form, the inability to detect an EPR signal for Cu(II) implied a strong antiferromagnetic interaction between the two Cu(II) centers, necessitating a structure where the two ions are in close proximity (3–4 Å). This model has been refined by detailed chemical and spectroscopic data which exclude cysteine sulfur ligation at the copper site.[3] Later, EXAFS studies have implied that the ligand environment around each copper consists of two[4] or three[5] histidine (imidazole) groups with an endogenous ligand (tyrosine or hydroxide) bridging the copper centers, which are separated by 3.67[4] or 3.55 Å[5] in the oxyhemocyanin. Very recently, the structure of *Panulirus interruptus* desoxyhemocyanin has been elucidated at 3.2-Å resolution[6] and reveals that each copper is bound to three histidine residues; it also shows that there is no evidence for a bridging protein between the coppers separated by a distance of 3.8 ± 0.4 Å (which corresponds well with Spiro's model[4]), although a small endogenous ligand could not be excluded.

Lacking this latter information, we initiated our research in this area by the construction of a binucleating ligand using a *p*-xylyl backbone, which, molecular models showed, would allow close approach of the two copper ions. The choice of a $NS_2O$ 12-membered macrocycle was determined by three considerations: (a) the $NS_2O$ donor set appeared suitable to reproduce in the Cu(II) complex certain important parts of the visible spectrum of the oxidized form of hemocyanin, particularly the absorption at 680 nm; (b) the $NS_2O$ donor set might be expected to afford strong complexation of *both* Cu(I) and Cu(II), possessing both soft (S) and hard (O, N) donors in the same ligand; (c) the *12*-membered macrocycle would permit strong complexation without totally encapsulating the metal ion, thereby leaving the metal exposed on one face of the cycle and thus accessible to reaction (with, e.g., CO and $O_2$).[7a] The ligand is shown in Figure 1; in the "earmuff" or closed configuration **1a** the metals are in close proximity, but in the open arrangement **1b**, they are distant. Structures of both types have already been reported.[7b]

In this paper we describe the synthesis and the characterization of the binucleating ligand L and its mononucleating analogue L′ and the complexes formed with Cu(II) and Cu(I). The degree

**Scheme I.** Synthesis of the $NS_2O$ Crown Based on Methods A and B




of interaction between sites has been probed by measurements of stability constants as well as kinetic studies. The "binuclear effect" induced by L has been evaluated by comparison with parallel studies using L′. Further papers will deal with the detailed magnetic and electrochemical properties of these binuclear species, the interaction of $O_2$ with the $Cu^I_2$ complexes, and the specific effect of imidazole on reactions with molecular oxygen.

## Experimental Section

**Materials.** All experiments involving the syntheses of ligands and Cu(I) complexes were carried out under an inert atmosphere of prepurified nitrogen with Schlenk glassware or in an argon-filled Vacuum Atmospheres glovebox. Oxygen- and peroxide-free solvents were obtained by conventional distillation under nitrogen in the presence of the appropriate reducing agents. Butanone was dried over $CaSO_4$ and distilled under $N_2$ with use of a Vigreux column. Propylene carbonate (Merck) was dried over CaO and distilled under reduced pressure at 70 °C. Acetonitrile was refluxed for 2 h over $CaH_2$ and distilled under $N_2$. Special care was taken in the conventional degassing method (freeze–pump–thaw) whenever Cu(I) complexes were involved. Elemental analyses were performed by the CNRS Microanalytical Laboratory at Lyon and Strasbourg. Melting points were determined on a Thomas Hoover capillary apparatus and were uncorrected.

**Spectroscopic Methods and Magnetic Measurements.** Electronic diffuse-reflectance spectra were recorded with a Beckman Acta C III instrument, with magnesium carbonate as reference for solid samples. The UV/visible spectra of solutions were obtained, with use of a Cary 219 or a Jobin Yvon Duospac spectrophotometer with quartz cells. Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer (Nujol mulls, reported in $cm^{-1}$). NMR spectra were recorded on a Varian EM 360 A ($^1H$) and a Bruker SY 200 or a Cameca 250 spectrometer ($^1H$, $^{13}C$, $^{31}P$). Chemical shifts $\delta$ are referenced to $(CH_3)_4Si$ ($^1H$, $^{13}C$) or $H_3PO_4$ ($^{31}P$) in organic solvents, and coupling constants are reported in hertz. Multiplicities are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

The EPR experiments were performed with a Bruker ER 420 X-band spectrometer provided with a $TE_{104}$ cavity, a NMR gauss meter, a frequency meter, and a BNC 12 computer for data handling facilities. The magnetic susceptibility measurements were carried out at room temperature with a Faraday-type magnetometer equipped with a Sartorius electronic balance. Platinum metal was used as a susceptibility standard. The applied magnetic fields were in the range 500–7000 G. Diamagnetic corrections were applied for all nonmetallic atoms, with use of a direct measurement for the ligand L ($-320 \times 10^{-6}$ $cm^3$ $mol^{-1}$) and the tabulated values of Pascal's constants for the other atoms.

**Conductometric Measurements.** Electrolytic conductance measurements were made on $5 \times 10^{-4}$ M solutions in nitrobenzene, with a YSI Model 31 conductimeter and a conventional cell that was previously calibrated with an aqueous solution of potassium chloride (0.01 N).

**Thermodynamic and Kinetic Measurements.** All measurements were carried out at 25 ± 0.1 °C. The ionic strength was maintained at 0.1

(3) Wurzbach, J. A.; Grunthaner, P. J.; Dooley, D. M.; Gray, H. B.; Grunthaner, F. J.; Gay, R. R.; Solomon, E. I. *J. Am. Chem. Soc.* **1977**, *99*, 1257.
(4) Brown, J. M.; Powers, L.; Kincaid, D.; Larrabee, J. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 4210.
(5) Co, M. S.; Hodgson, K. O.; Eccles, T. K.; Lontie, R. *J. Am. Chem. Soc.* **1981**, *103*, 984.
(6) (a) Gaykema, W. P. J.; Hol, W. G. J.; Vereijken, J. M.; Soeter, N. M.; Bak, H. J.; Beintema, J. J. *Nature (London)* **1984**, *309*, 23. (b) Hol, W. G. J.; Volbeda, A. *Rev. Port. Quim.* **1985**, *27*, 42.
(7) (a) Bulkowski, J. E.; Burk, P. L.; Ludmann, M.-F.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498. (b) Burk, P. L.; Osborn, J. A.; Youinou, M. T.; Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1273.

M with lithium nitrate in aqueous solutions and with lithium perchlorate in propylene carbonate solutions.

pH measurements were carried out in an Ingold 5-mL thermostated cell with a Beckman 39099E3 glass electrode and a Tacussel C 10 calomel reference electrode saturated in KCl, connected to a Tacussel Aries 20000 voltmeter. A $1 \times 10^{-3}$ M nitric acid solution containing 0.099 M $LiNO_3$ was employed as a standard of hydrogen concentration ($-\log [H^+] = 3.00$).

Spectrophotometric and pH-metric data were calculated on a Univac 1110 computer.

Kinetic measurements were conducted with a Durrum D131 stopped-flow spectrophotometer equipped with a Datalab DL 905 transient recorder that was interfaced to a Olivetti P 652 microcomputer. This system and the computer programs for data treatment have been previously described.[8]

**Synthesis. 1. Ligands.** The ligands L and L′ have been synthesized by using the macrocyclic amine 1-oxa-4,10-dithia-7-azacyclododecane as a common intermediate by the two procedures summarized in Scheme I and described respectively below.

**Method A** is a modified version of the synthesis previously described.[9] The amine bromide $H_2N(CH_2CH_2Br)_2Br$ was prepared according to a literature method.[10] In a three-necked 6-L round-bottom flask fitted with a magnetic stirrer and reflux condenser, 0.06 mol (18.7 g) of $H_2N(CH_2CH_2Br)_2Br$ was dissolved in 1200 mL of dry degassed isopropyl alcohol (distilled on $CaH_2$). One equivalent of sodium isopropoxide (1.38 g of Na in 200 mL of hot isopropyl alcohol) was added at once. The solution mixture was stirred for 1 h. In the meantime, in a separate two-necked 2-L round-bottom flask fitted with a magnetic stirrer, 0.06 mol of $O(CH_2CH_2SH)_2$ (7.45 mL) and 800 mL of degassed isopropyl alcohol were combined under nitrogen. Two equivalents of sodium isopropoxide (2.76 g of Na in 400 mL of hot isopropyl alcohol) was added at once, and the reaction mixture was stirred for 20 min. To the solution of $HN(CH_2CH_2Br)_2$ was added under $N_2$, with rapid stirring, the freshly prepared solution of the thiolate over a period of 30 min. The stirred reaction mixture was refluxed for 2 days. The solvent was then distilled until dryness, and the crude product was taken up in 300 mL of 1 N NaOH. The suspension was extracted with toluene ($4 \times 100$ mL). The combined extracts were dried over $K_2CO_3$, and the solvent was evaporated to give 8.50 g of a yellowish semisolid, which was then dissolved in several portions of hexane ($5 \times 75$ mL). After evaporation of the solvent, 4 g of the white pure amine was obtained. A further amount of the macrocyclic amine was collected from the insoluble oily crude product after separation by column chromatography (alumina II, III; 130 g in hexane); the elution was started with hexane (150 mL) and then with dichloromethane (1200 mL). This procedure afforded 4.7 g (38%) of pure product (TLC, alumina plates, $CH_2Cl_2$, 2% MeOH detected with iodine) as a white solid. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 3.56 (t, 4 H, $OCH_2CH_2S$), 2.74 (m, 13 H, NH + $NCH_2CH_2S$ + $OCH_2CH_2S$).

**Method B** is based on the formation of the tosylated macrocycle, followed by its detosylation.

**(*p*-Tolylsulfonyl)bis(2-((*p*-tolylsulfonyl)oxy)ethyl)amine** was prepared by standard methods[11] and was obtained after recrystallization from ethanol as a white solid (75% yield), mp 82–83 °C (lit.[12] mp 65–67 °C). $^1H$ NMR (60 MHz, $CDCl_3$) $\delta$ 7.9–7.2 (m, 12 H, Ph (tosyl)), 4.12 (t, 4 H, $NCH_2CH_2OTs$), 3.38 (t, 4 H, $NCH_2CH_2OTs$), 2.45 (s, 6 H, 2 $CH_3$ (tosyl)), 2.40 (s, 3 H, $CH_3$ (tosyl)).

**The macrocycle 7-(*p*-tolylsulfonyl)-1-oxa-4,10-dithia-7-azacyclododecane** was obtained by a synthetic route based on the general procedure of Richman and Atkins.[13] 3-Oxapentane-1,5-dithiol (6.9 g, 0.05 mol) in 125 mL of dry methanol was converted under nitrogen into the disodium salt by addition of a sodium methoxide solution prepared from sodium (2.3 g, 0.1 mol) in 125 mL of methanol. Evaporation of methanol under reduced pressure gives the disodium salt, which was used without further purification.

$O(CH_2SNa)_2$ (9.1 g, 0.05 mol) was added under nitrogen to 500 mL of degassed DMF in a 3-L three-necked round-bottom flask equipped with a mechanical stirrer, an addition funnel, and a heating mantle. The solution was heated to 90 °C with stirring, and the tritosylate derivative (28.4 g, 0.05 mol) in 250 mL of DMF was added dropwise over 1 h, during which the solution became yellow. The reaction mixture was allowed to cool to room temperature and stirred overnight. DMF was then removed under reduced pressure, the residue was taken up in water (500 mL), and the product was extracted four times with 200-mL portions of chloroform. The organic solvent was evaporated, and a yellow oily material was obtained (21 g). After separation by column chromatography (alumina II, III; 600–700 g in toluene; elution with toluene and then a mixture of toluene/dichloromethane), a white pure solid (10.8 g, 60%) was obtained. $^1H$ NMR (200 MHz, $CD_2Cl_2$): $\delta$ 7.63 (d, 2 H, protons meta to $CH_3$ in tosyl group), 7.31 (d, 2 H, protons ortho to $CH_3$ in tosyl group), 3.68 (t, 4 H, $OCH_2CH_2S$), 3.47 (m, 4 H, $NCH_2CH_2S$), 2.84 (m, 4 H, $NCH_2CH_2S$), 2.68 (t, 4 H, $OCH_2CH_2S$), 2.41 (s, 3 H, $PhCH_3$).

**The detosylation of the macrocycle** was achieved according to the general procedure[14] based on the cleavage of sulfonamides with sodium naphthalene in 1,2-dimethoxyethane (DME). A 50-mL DME solution 1 M in anion radical was prepared as previously described.[14] The blue solution of the anion radical was added dropwise with a gastight syringe under nitrogen to a cooled (−15 °C) degassed solution of the tosylate macrocycle (1.8 g, 5 mmol) in DME (30 mL). The color faded away rapidly at the beginning of the addition and toward the end of the reaction more slowly. The endpoint was determined as follows: samples were taken from the reaction mixture; the filtered solution was reduced to dryness, and the $^1H$ NMR spectrum of the residue was recorded in $CDCl_3$; as soon as the characteristic aromatic pattern of the tosylate groups disappeared, no more sodium anthracene solution was added. The reaction mixture was allowed to stand at −15 °C for 45 min and then to warm slowly to room temperature. The precipitate was then filtered off and washed twice with 10-mL portions of DME. The combined yellowish DME solutions were mixed with 1 N HCl (25 mL), and the clear acid solution obtained after filtration of the precipitate was extracted three times with 100-mL portions of $CH_2Cl_2$. The water phase was very carefully made basic with LiOH and cooled. The cloudy solution was extracted eight times with 100-mL portions of $Et_2O$, and the combined extracts were dried over $MgSO_4$. After evaporation of $Et_2O$, and standing overnight at 0 °C, a semisolid was obtained. The NMR data did not show any significant impurity, and the product was used without any further purification. However, in our hands, this method was difficult to reproduce, offering significantly variable yields (from 20% to 60%).

**Preparation of 1,4-Bis((1-oxa-4,10-dithia-7-azacyclododec-7-yl)methyl)benzene, L.** The diamide was prepared according to the following procedure. A solution of terephthaloyl chloride, $C_6H_4$-1,4-$(COCl)_2$ (2.3 g, 11.35 mmol) (recrystallized from hexane), in 100 mL of dry benzene was added dropwise over a period of 30 min under nitrogen to a vigorously stirred solution of the macrocyclic amine (4.7 g, 22.7 mmol) in 250 mL of deoxygenated benzene containing 4.2 mL of distilled triethylamine and maintained at 0 °C by external cooling. The mixture was then refluxed for 4 h, cooled overnight, and filtered. The filtrate was washed with 5% aqueous $NaHCO_3$ ($2 \times 100$ mL) and water (100 mL) and dried over $K_2CO_3$. Benzene was removed under reduced pressure to give a colorless solid, which was used without any further purification (6.1 g, 99%). $^1H$ NMR (200 MHz, $CD_2Cl_2$): $\delta$ 7.37 (s, 4 H, aromatic), 3.74 (m, 16 H, $OCH_2CH_2S$ + $NCH_2CH_2S$), 2.94 and 2.75 (t + m, 16 H, $SCH_2CH_2O$ + $SCH_2CH_2N$).

The diamide was reduced according to the general procedure described by Brown.[15] $BH_3{\cdot}SMe_2$ (17 mL, 47 mmol, 2 M solution in THF from Aldrich, previously titrated by reaction with $H_2O$ and measurement of $H_2$ evolution) in 150 mL of THF was added dropwise to the diamide (6.1 g, 11.2 mmol) suspended in dry THF (200 mL) under nitrogen at 0 °C. The mixture was stirred for 30 min at room temperature and refluxed for 2.5 h. The flask was allowed to cool to room temperature, and 12 mL of 6 M HCl was added. The solvent was removed by distillation at atmospheric pressure. Concentrated sodium hydroxide was added until pH 9; the aqueous phase was extracted three times with $CH_2Cl_2$ ($3 \times 70$ mL), and the combined extracts were dried over $K_2CO_3$. $CH_2Cl_2$ was removed under vacuum, and 6.17 g of crude product was obtained. The sample was then column chromatographed on alumina (alumina II, III) prepared with hexane. The product was eluted with hexane/$CH_2Cl_2$ (4:1) and then hexane/$CH_2Cl_2$ (1:1) and pure $CH_2Cl_2$. A 2.3-g (40%) amount of pure material was obtained for each chromatographic separation (TLC, alumina plates, 3:1 $Et_2O$/hexane); mp 107 °C. $^1H$ NMR (200 MHz, $CD_2Cl_2$): $\delta$ 7.25 (s, 4 H, aromatic), 3.76 (t, 8 H, $OCH_2CH_2S$), 3.63 (s, 4 H, $NCH_2Ph$), 2.84 (m, 16 H, $SCH_2CH_2N$), 2.72 (t, 8 H, $OCH_2CH_2S$). $^{13}C\{^1H\}$ NMR (200 MHz, $CD_2Cl_2$): $\delta$ 138.95 (s, 2 C, $NCH_2C$ (aromatic)), 128.96 (s, 4 C, CH (aromatic)), 75.01 (s, 4 C, $OCH_2CH_2S$), 60.07 (s, 2 C, $NCH_2Ph$), 52.21 (s, 4 C, $NCH_2CH_2S$), 31.21 and 28.78 (2 s, $2 \times 4$ C, $SCH_2CH_2N$ and $SCH_2CH_2O$). Anal.

(8) (a) Zare, K.; Lagrange, J.; Lagrange, P. *Inorg. Chem.* **1979**, *18*, 568. (b) Collin, J. P.; Lagrange, P. *Bull. Soc. Chim. Fr.* **1976**, 1304.
(9) Black, D. St.C.; McLean, I. A. *Aust. J. Chem.* **1971**, *24*, 1381.
(10) Bobranski, B.; Jakobiec, T.; Preliez, D. *Acta Pol. Pharm.* **1955**, *12*, 195.
(11) Marvel, C. S.; Sekera, V. C. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. 3, p 366.
(12) Peacock, D. H.; Dutta, U. C. *J. Chem. Soc.* **1934**, 1903.
(13) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268.
(14) Sungchul Ji; Gortler, L. B.; Waring, A.; Battisti, A.; Bank, S.; Closson, W. D.; Wriede, P. *J. Am. Chem. Soc.* **1967**, *89*, 5311.
(15) Brown, H. C.; Heim, P. *J. Org. Chem.* **1973**, *38*, 912.

Calcd for $C_{24}H_{40}N_2O_2S_4$: C, 55.77; H, 7.80; n, 5.42; S, 24.81. Found: C, 55.5; H, 7.7; N, 5.4; S, 24.9.

**Preparation of ((1-Oxa-4,10-dithia-7-azacyclododec-7-yl)methyl)benzene, L'.** The ligand L' was obtained in a manner analogous to that reported for L. To a solution of the macrocyclic amine (1.78 g, 8.61 mmol) in benzene (40 mL) and triethylamine (1.5 mL) was added dropwise under nitrogen a solution of benzoyl chloride (1 mL, 8.61 mmol) in benzene (20 mL). The reaction mixture was treated as before. The oily crude amide was then column chromatographed on silica gel prepared with hexane. The product was eluted with hexane/diethyl ether (1:1) and then pure ether. A 1.8-g (67%) amount of pure colorless material was obtained. Then the amide was reduced with $BH_3{\cdot}SMe_2$, followed by the same workup procedure as for the diamide. Unlike with L, further purification of L' was achieved by precipitation of the amine chloride after bubbling gaseous HCl through the stirred solution of L' in tetrahydrofuran. The white precipitate was triturated with a rod, kept at 0 °C overnight, filtered off, washed with hot THF, and dried in vacuo. A total of 1.9 g (67%) of pure material was obtained. Anal. Calcd for $C_{15}H_{24}NOS_2Cl$: C, 53.96; H, 7.19; N, 4.19; Cl, 10.62. Found: C, 53.9; H, 7.6; N, 4.3; Cl, 10.3.

The free amine was liberated from an aqueous solution of the hydrochloride by addition of sodium hydroxide and subsequent extraction with $CH_2Cl_2$. After evaporation of the solvent, a clear colorless oil was obtained. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.34 (m, 5 H, aromatic), 3.76 (t, 4 H, $OCH_2CH_2S$), 3.68 (s, 2 H, $NCH_2Ph$), 2.88 (s, 8 H, $SCH_2CH_2N$), 2.72 (t, 4 H, $OCH_2CH_2S$). $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$): $\delta$ 139.29 (s, 1 C, $NCH_2C$ (aromatic)), 128.42 and 128.0 (2 s, 2 × 2 C, CH (aromatic)), 126.76 (s, 1 C, CH (aromatic)), 74.31 (s, 2 C, $OCH_2CH_2S$), 59.41 (s, 1 C, $NCH_2Ph$), 51.36 (s, 2 C, $NCH_2CH_2S$), 30.46 and 28.07 (2 s, 2 × 2 C, $SCH_2CH_2N$ and $SCH_2CH_2O$).

**2. Preparation of Copper(II) Complexes. (a) Preparation of $[Cu_2L](BF_4)_4{\cdot}6H_2O$ (1).** A 0.13-g (0.25-mmol) amount of the ligand L was dissolved in 2 mL of warm propylene carbonate (PC). To the cooled solution of the ligand was added 0.177 g (0.51 mmol) of $Cu(BF_4)_2{\cdot}6H_2O$ in 2 mL of propylene carbonate. Vapor diffusion of dichloromethane into the resultant dark green solution gave, after 2 days, crystals of the compound, which were filtered, washed several times with a mixture of $CH_2Cl_2$ and PC (5:1) and finally with pure $CH_2Cl_2$, and dried in vacuo (0.18 g, 65%). Anal. Calcd for $C_{24}H_{40}N_2O_2S_4Cu_2B_4F_{16}{\cdot}6H_2O$: C, 26.22; H, 4.77; N, 2.55; S, 11.67; Cu, 11.56; F, 27.65. Found: C, 26.58; H, 4.56; N, 2.31; S, 11.51; Cu, 11.58; F, 26.84. Optical spectrum (PC; $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)): 670 (1030), 390 (8630), 315 (4100), 275 (sh). Magnetic moment: $\mu_{eff}$(293 K) = 1.85 $\mu_B$. EPR spectrum (solid state, 20 °C): $g$ = 2.099.

**(b) Preparation of $[Cu_2(\mu\text{-}OH)L](BF_4)_3{\cdot}PC$ (2a).** After dissolution of 0.258 g (0.5 mmol) of ligand L and 0.345 g (1 mmol) of $Cu(BF_4)_2{\cdot}6H_2O$ in propylene carbonate, the solutions were combined (total volume 5 mL) and the resultant dark green solution was kept in a drybox over 3-Å molecular sieves, which were changed three times over a period of 3 days. After the final filtration, the solution was transferred into an antechamber containing distilled tetrahydrofuran. Dark green crystals came out after standing 1 month in the drybox (0.248 g, 48%). Anal. Calcd for $C_{24}H_{41}N_2O_3S_4Cu_2B_3F_{12}{\cdot}C_4H_6O_3$: C, 32.86; H, 4.63; N, 2.74; Cu, 12.41; F, 22.27. Found: C, 33.12; H, 4.74; N, 2.40; Cu, 12.00; F, 22.54. Optical spectrum (PC; $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)): 685 (970), 585 (sh), 447 (6360), 375 (8500), 315 (2775). Magnetic moment: $\mu_{eff}$(293 K) = 0.48 $\mu_B$/Cu. EPR spectrum (solid state, 20 °C): $\Delta m$ = 2 at $H$ = 1515 G and $\Delta m$ = 1 at $H$ = 3187 G; $J$ = −375 $cm^{-1}$ (determined from the temperature variation of the $\Delta m$ = 2 signal). IR spectrum (Nujol mull, $cm^{-1}$): CO stretch (from PC) 1780 (s) (cf. neat PC (KBr windows) at 1790 (s)).

**(c) Preparation of $[Cu_2(\mu\text{-}OH)L](BF_4)_3{\cdot}PC{\cdot}H_2O{\cdot}0.5EtOAc$ (2b).** This method resulted from an attempt of synthesis of a bridging imidazolate dimer complex and was found to give a $\mu$-hydroxo complex. To a warm solution of 0.388 g (0.75 mmol) of ligand L in 15 mL of distilled PC was added 0.518 g (1.5 mmol) of $Cu(BF_4)_2{\cdot}6H_2O$ as a solid. When the solid dissolved, the solution turned dark green. A solution of imidazole, 0.05 g (0.75 mmol), in PC in the ratio ImH:L = 1:1 was added to the previous mixture. The total solution (~20 mL) was filtered off. Vapor diffusion of distilled (over $P_2O_5$) ethyl acetate or alternatively $CH_2Cl_2$ produced dark green crystals after 6 weeks (0.59 g, 72%). Anal. Calcd for $C_{24}H_{41}N_2O_3S_4Cu_2B_3F_{12}C_4H_6O_3{\cdot}H_2O{\cdot}0.5C_4H_8O_2$: C, 33.19; H, 4.92; N, 2.58; S, 11.82; Cu, 11.71; F, 21.00. Found: C, 33.28; H, 4.79; N, 2.77; S, 11.83; Cu, 11.31; F, 21.45. Optical spectrum (PC; $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)): 685 (995), 585 (sh), 447 (6200), 375 (8520), 315 (2360). EPR spectrum (solid state, 20 °C): $\Delta m$ = 2 at $H$ = 1500 G and $\Delta m$ = 1 at $H$ = 3198 G; $J$ = 425 $cm^{-1}$ (determined by the same method as above). IR spectrum (Nujol mull, $cm^{-1}$): CO stretch (from PC) 1790, 1750 (s); the peak 1750 of the doublet overlapped the CO stretch from EtOAc (at 1740 as a neat liquid); C–O–C stretch (from EtOAc) 1240 (w). Alternatively when $CH_2Cl_2$ is used as cosolvent, its presence is detected by chloride analysis (Anal. Calcd for $0.5CH_2Cl_2$ solvate: Cl, 3.27. Found: Cl, 3.27).

**(d) Preparation of $[CuL'](BF_4)_2{\cdot}3H_2O$ (3).** To a solution of 0.144 g (0.48 mmol) of the ligand L' in 3 mL of PC was added with constant stirring a 2-mL solution of $Cu(BF_4)_2{\cdot}6H_2O$ (0.167 g, 0.48 mmol) in PC. Vapor diffusion of dichloromethane into the solution mixture gave after 2 weeks a crystalline compound. The crystals were collected and washed with $CH_2Cl_2$/PC (5:1) and pure $CH_2Cl_2$ (yield 0.21 g, 75%). Anal. Calcd for $C_{15}H_{23}NOS_2CuB_2F_8{\cdot}3H_2O$: C, 30.60; H, 4.96; N, 2.39; S, 10.89. Found: C, 30.31; H, 4.50; N, 2.20; S, 11.20. Optical spectrum (PC; $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)): 675 (475), 380 (4620), 307 (1900).

**3. Preparation of Copper(I) Complexes.** Tetrakis(acetonitrile)copper(I) tetrafluoroborate was synthesized from $Cu_2O$ and borontrifluoride etherate in acetonitrile by the method of Meerwein;[16] the perchlorate (or hexafluorophosphate) salt was obtained from $Cu_2O$ and $HClO_4$ (or $HPF_6$) described by Hemmerich;[17] the triflate (OTf) derivative was prepared according to Kochi.[18]

**(a) Preparation of $[Cu_2L]X_2{\cdot}n$PC (X = $BF_4$, $ClO_4$, $PF_6$) (4a–c).** To a degassed warm solution of $[Cu(CH_3CN)_4](BF_4)$ (1.83 g, 5.8 mmol) in butanone (200 mL) was added dropwise via a cannula under nitrogen a warm solution of L (1.00 g, 1.94 mmol) in butanone (70 mL) with stirring and external heating of the reaction flask at about 50 °C. A fluffy precipitate formed immediately. The reaction mixture was heated for an extra 30-min period after the end of the addition and then cooled to room temperature. Most of the solvent was then removed after decantation; the greenish precipitate was collected by filtration, washed twice with 20-mL portions of degassed butanone, and dried under vacuum (1.46 g, 90%). The product contained free butanone as evidenced by infrared data ($\nu_{C=O}$ at 1705 $cm^{-1}$ in Nujol mull (cf. neat butanone, KBr windows, at 1710 $cm^{-1}$)) and NMR data (200 MHz, $CD_3CN$; $\delta$ 0.94 (t, 3 H, $CH_3CH_2$), 2.05 (s, 3 H, $CH_3CO$), 2.42 (q, 2 H, $CH_3CH_2$)) and confirmed by elemental analysis for the perchlorate derivative, for instance (Anal. Calcd for $C_{24}H_{40}N_2O_{10}S_4Cu_2Cl_2{\cdot}0.4C_4H_8O$: C, 35.27; H, 5.00; N, 3.21. Found: C, 35.14; H, 5.05; N, 2.97). Whenever a perfectly pure sample was needed, the slightly oxidized compound was then taken up in the minimum amount of warm degassed propylene carbonate; the copper(II) present was reduced by adding small portions of copper metal (previously activated by HCl and washed with aceton) until a colorless solution was obtained, with vigorous stirring. After filtration of Cu(0), degassed ethyl acetate was slowly added to the PC filtrate in the ratio 10:1. The white solid was then filtered, washed with EtOAc, and dried under vacuum (yield 1.24 g, 52%). Anal. Calcd for $C_{24}H_{40}N_2O_2S_4Cu_2B_2F_8{\cdot}4C_4H_6O_3$: C, 39.19; H, 5.26; S, 10.46. Found: C, 39.16; H, 5.20; S, 10.52. The presence of free PC is confirmed by IR ($\nu_{C=O}$ at 1785 $cm^{-1}$) and $^1H$ NMR data (200 MHz, $CD_3CN$; $\delta$ 1.41 (d, 3 H, $CH_3$), 4.03 and 4.54 (2 t, 2 × 1 H, $CH_2CHCH_3$), 4.87 (m, 1 H, $CHCH_3$)). The amount of butanone present as well as propylene carbonate (combined sometimes with EtOAc) depended upon each preparation. $^1H$ NMR (200 MHz, $CD_3CN$): $\delta$ 7.35 (s, 4 H, aromatic), 3.66 (s, 8 H, $OCH_2CH_2S$), 3.96 (s, 4 H, $NCH_2Ph$), 3.02 (s, 8 H, $NCH_2CH_2S$), 2.91 (m, 8 H, $SCH_2CH_2O$), 2.70 (s, 8 H, $SCH_2CH_2N$). $^{13}C\{^1H\}$ NMR (250 MHz, $CD_3CN$): 134.46 (s, 2 C, $NCH_2C$ (aromatic)), 132.14 (s, 4 C, CH (aromatic)), 66.72 (s, 4 C, $OCH_2CH_2S$), 58.98 (s, 2 C, $NCH_2Ph$), 52.01 (s, 4 C, $NCH_2CH_2S$), 33.82 and 33.04 (2 s, 2 × 4 C, $SCH_2CH_2N$ and $SCH_2CH_2O$).

**(b) Preparation of $[Cu_2L](OTf)_2$ (4d).** The previous procedure could also be used; however, it was more convenient to synthesize this very air-sensitive compound in a drybox, by using benzene (distilled on sodium and benzophenone) as solvent and $(CuOTf)_2C_6H_6$ as copper(I) source. The ligand L (0.35 g, 0.67 mmol) in warm degassed benzene (20 mL) was added dropwise to a solution of $(CuOTf)_2C_6H_6$ (0.51 g, 1 mmol) in benzene (50 mL) with stirring. The white precipitate formed was immediately collected by filtration, washed twice with 20-mL portions of benzene, and dried under vacuum (0.52 g, 82%). The NMR data were identical with the previous ones. This compound was very soluble in propylene carbonate.

**(c) Preparation of $[Cu_2L(Ph_3P)_2](BF_4)_2$ (5).** The addition of a solution of $Ph_3P$ (0.027 g, 0.1 mmol) in acetonitrile (1 mL) to a stirred suspension of $[Cu_2L](BF_4)_2{\cdot}0.9PC$ (0.041 g, 0.045 mmol) in acetonitrile (2 mL) under nitrogen yielded a clear colorless solution from which, after evaporation of the solvent until dryness, a white solid was obtained. This material was collected, washed with pentane, and used without any further purification (no impurity detectable by NMR). $^1H$ NMR (200

(16) Meerwein, H.; Hederich, V.; Wunderlich, K. *Arch. Pharm. Ber. Dtsch. Pharm. Ges.* **1958**, *291*, 541.
(17) Hemmerich, P.; Sigwart, C. *Experientia* **1963**, *19*, 488.
(18) Solomon, R. G.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1972**, 559; *J. Am. Chem. Soc.* **1973**, *95*, 1889.

MHz, $CD_3CN$): δ 7.48 (m, 30 H, Ph ($Ph_3P$)), 7.04 (s, 4 H, aromatic (L)), 3.70 (s, 8 H, $OCH_2CH_2S$), 3.63 (s, 4 H, $NCH_2Ph$), 3.11 (s, 8 H, $NCH_2CH_2S$), 2.96 (s, 8 H, $SCH_2CH_2O$), 2.73 (s, 8 H, $SCH_2CH_2N$). $^{31}P$ NMR (200 MHz, $CD_3CN$): δ 2.50 (s, $Ph_3P$). No signal from free triphenylphosphine at −4.26 ppm was detectable.

**(d) Preparation of [CuL′]X (X = $BF_4$, $ClO_4$) (6).** To a carefully degassed solution of $[Cu(CH_3CN)_4](BF_4)$ (0.190 g, 0.60 mmol) in butanone (10 mL) was added dropwise under nitrogen a solution of L′ (0.180 g, 0.60 mmol) in butanone (10 mL). The resultant greenish solution was reduced with copper metal (activated with concentrated HCl and washed with acetone) and stirred for 15 min. The unreacted Cu(0) was removed by filtration, and to the colorless filtrate was added cold degassed diethyl ether, yielding the precipitation of a white product, which was filtered off and dried under vacuum (0.290 g, 99%). The analysis of the NMR spectrum indicated the presence of 0.4 mol of some starting material $[Cu(CH_3CN)_4](BF_4)$ for 1 mol of the desired product. $^1H$ NMR (90 MHz, $Me_2SO$-$d^6$): δ 2.07 (s, $CH_3CN$). This material was taken up in warm degassed tetrahydrofuran; the THF solution was evaporated until the appearance of slight turbidity and degassed diethyl ether was slowly added. The expected white precipitate formed; it was filtered off, washed with diethyl ether, dried under vacuum, and stored in the dark. Anal. Calcd for $C_{15}H_{23}NOS_2CuBF_4$: C, 40.23; H, 5.18; N, 3.18. Found: C, 39.90; H, 5.08; N, 3.40. $^1H$ NMR (200 MHz, $Me_2SO$-$d^6$): δ 7.37 (s, 5 H, aromatic), 3.93 (s, 2 H, $NCH_2Ph$), 3.69 and 3.59 (m, br, 4 H, $OCH_2CH_2S$), 3.15 and 2.99 (2 m, br, 2 × 4 H, $SCH_2CH_2N$), 2.70 and 2.63 (m, br, 4 H, $SCH_2CH_2O$). $^{13}C\{^1H\}$ (200 MHz, $Me_2SO$-$d^6$): δ 133.13 (s, 1 C, $NCH_2C$ (aromatic)), 131.10 and 128.24 (2 s, 2 × 2 C, CH (aromatic)), 127.72 (s, sh, 1 C, CH (aromatic)), 64.44 (s, 2 C, $OCH_2CH_2S$), 56.88 (s, 1 C, $NCH_2Ph$), 49.81 (s, 2 C, $NCH_2CH_2S$), 32.08 and 31.52 (2 s, 2 × 2 C, $SCH_2CH_2N$ and $SCH_2CH_2O$).

**(e) Synthesis of $[Cu_2L'_3]X_2$ (X = $BF_4$, $ClO_4$) (7).** A degassed solution of L′ (0.220 g, 0.74 mmol) in butanone (10 mL) was added dropwise under nitrogen to a warm butanone solution (15 mL) containing $(Cu(CH_3CN)_4)BF_4$ in a quantity such that the ratio $L':Cu^+ \geq 1.2:1$ (0.190 g, 0.6 mmol). The reaction mixture was stirred for $^1/_2$ h at room temperature. The fluffy green precipitate formed in a small amount was filtered off and discarded. The volume of the colorless filtrate was reduced to about 5–10 mL, and the reaction flask was maintained at 0 °C overnight. White crystals precipitated out and were filtered off and dried under vacuum (0.250 g, 57% (based on ligand)). Anal. Calcd for $C_{45}H_{69}N_3O_3S_6Cu_2B_2F_8$: C, 45.30; H, 5.83; N, 3.52; S, 16.13; Cu, 10.65; F, 12.74. Found: C, 45.34; H, 5.60; N, 3.50; S, 15.71; Cu, 10.23; F, 12.6. $^1H$ NMR (250 MHz, $Me_2SO$-$d^6$): δ 7.35 (s, 5 H, aromatic), 3.82 (s, 2 H, $NCH_2Ph$), 3.67 (t, 4 H, $OCH_2CH_2S$), 3.00 (t, 4 H, $NCH_2CH_2S$), 2.90 (t, 4 H, $SCH_2CH_2O$), 2.72 (t, 4 H, $SCH_2CH_2N$). $^{13}C\{^1H\}$ (200 MHz, $Me_2SO$-$d^6$): δ 135.20 (s, 1 C, $NCH_2C$ (aromatic), 129.97 and 127.99 (2 s, 2 × 2 C, CH (aromatic)), 127.41 (s, 1 C, CH (aromatic)), 67.41 (s, br, 2 C, $OCH_2CH_2S$), 57.62 (s, 1 C, $NCH_2Ph$), 50.23 (s, 2 C, $NCH_2CH_2S$), 31.10 and 30.71 (2 s, 2 × 2 C, sh 2:1, $SCH_2CH_2N$ and $SCH_2CH_2O$).

## Results and Discussion

**(a) Synthesis and Properties of the Ligands L and L′ as well as the Cu(II) and Cu(I) Complexes.** The ligand syntheses were relatively straightforward although for reasons yet undetermined the cyclization step and the Na/naphthalene reaction of the tosylate gave occasionally low yields. The ligands have been synthesized via the macrocycle 1-oxa-4,10-dithia-7-azacyclododecane as a common intermediate by two procedures as shown in Scheme I.

The first method, following Black and McLean,[9] initially in our hands gave low overall yields of this macrocycle. Consequently, we attempted to improve on this published synthesis as well as develop a new method involving cyclization of a tosylate derivative. Method A is essentially a modification of the published procedure by simply using isopropyl alcohol instead of methanol in the cyclization step, which we find markedly improves the overall yield (from 18% to 38%). The alternative route (method B) is based on the condensation of the tritosylate derivative and of the thiolate in DMF at 90 °C, which interestingly allows high-dilution techniques to be avoided.[9] The detosylation step by treatment with sodium anthracene anion radical gives the expected macrocyclic amine. However, because of the irreproducibility of the yields obtained by this procedure (from 20 to 60%), method A was adopted as a routine procedure.

By a classical acylation reaction in the presence of terephthaloyl chloride, $C_6H_4$-1,4-$(COCl)_2$, for L or benzoyl chloride, $C_6H_5COCl$, for L′, the corresponding amide is obtained in an excellent yield. The reduction in the presence of diborane gives the expected ligands L and L′.

The NMR data ($^1H$, $^{13}C$) (vide infra, part b) and UV/visible data (transparent λ > 250 nm at $c = 10^{-3}$ M in PC and λ > 225 nm at $c = 10^{-5}$ M in PC) of the ligands are unexceptional. A potentiometric study of both L and L′ is presented in part d.

Reaction of L with Cu(II) gave two products according to the conditions, the expected dark green complex $[Cu^{II}_2L](BF_4)_4 \cdot 6H_2O$ (**1**) and the singly bridged μ-hydroxo complex $[Cu^{II}_2(\mu\text{-}OH)L](BF_4)_3$ (**2**). These two complexes can be readily distinguished by their different physical properties, particularly electronic spectra and magnetism (vide infra). Notably, with L′ as ligand only the mononuclear **3** could be isolated, the bridged μ-hydroxo complex being neither isolated nor even detected in solution (see part e).

The syntheses of the Cu(I) complexes were more difficult than anticipated. Reactions of $[Cu(CH_3CN)_4]X$ (X = $BF_4$, $ClO_4$, $PF_6$) with L in butanone gave products that unvariably contained traces of copper(II) and variable amounts of solvent of crystallization. A perfectly colorless sample could be obtained by dissolution of the impure product in warm propylene carbonate, followed by reduction of the copper(II) present with activated copper metal, filtration, and precipitation of the required complex by adding ethyl acetate. The ratio of the solvent molecules (PC, EtOAc) present in the powdered solids was determined by NMR for each recrystallization. The triflate derivative could also be obtained in a satisfactory yield in benzene, by using the complex $(CuOTf)_2C_6H_6$ as copper(I) source. Extreme care was taken when handling all these complexes since they are very sensitive to oxidation.

The isolation of the copper(I) complexes of L′ requires carefully controlled conditions. For a $[Cu^I(CH_3CN)_4]X$:L ratio exactly equal to 1 (X = $BF_4$, $ClO_4$, OTf), the solid isolated from butanone is always contaminated with some $[Cu^I(CH_3CH)_4]^+$. A pure sample of [CuL′]X could be obtained by recrystallization from warm tetrahydrofuran/diethyl ether under anaerobic conditions. When the synthesis was carried out with a slight excess of L′ (e.g. $L':Cu^I \geq 1.2:1$), a white microcrystalline compound precipitated out readily, which was analyzed as a binuclear copper(I) complex with the formula $[Cu_2L'_3]X_2$ (**7**). The two compounds are however easily distinguished by their NMR patterns as well as their markedly different reactivity toward oxygen. The monomer species becomes easily greenish whereas the dimer is barely unstable in the presence of $O_2$. Furthermore, molar conductivities obtained on nitrobenzene solutions of **6** and **7** are different. Equivalent conductances are 22 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ at $6.6 \times 10^{-4}$ M for **6** and 51 $\Omega^{-1}$ cvm$^2$ mol$^{-1}$ at $5.5 \times 10^{-4}$ M for **7**, which are in agreement with the formulation of **6** as 1:1 electrolytes and **7** as 2:1 electrolytes (the values expected for $2 \times 10^{-4}$–$10^{-3}$ M solutions in nitrobenzene lie in the range 20–30 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for 1:1 electrolytes[19] and 50–60 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for 2:1 electrolytes[20]).

**(b) NMR Data of the Cu(I) and Cu(II) Complexes.** The $^1H$ NMR spectra of L and L′ are easily assigned by use of homonuclear decoupling. The spectrum of L and assignments are shown in Figure 2. On complexation with Cu(I), all resonances are somewhat displaced (see Experimental Section and Figure 2) but unexpectedly at room temperature the spectrum of $[Cu^I_2L]^{2+}$ shows some ligand resonances to be very broad in $CD_3CN$ or $(CD_3)_2SO$. A variable-temperature NMR study was carried out, and the results for $CD_3CN$ are presented in Figure 3. At +70 °C we observe four quasi-triplet resonances between δ 2.5 and 3.70 corresponding to four types of protons 1–4 of the ligand L assigned above. The benzylic protons 5 and aromatic protons 7 are shifted downfield to δ 3.96 and 7.35, respectively, and remain singlets. When the system is cooled, the resonances 1–4 are seen to broaden and separate into a more complex pattern at −40 °C. Identical results are obtained with $(CD_3)_2SO$ as solvent although the coalescence temperature is ca. 20 °C higher in this solvent. The mononuclear complex $[CuL']^+$ (**6**) exhibits the same phe-

(19) Lewis, J.; Nyholm, R. S.; Phillips, D. J. *J. Chem. Soc.* **1962**, 2177.
(20) Gill, N. S.; Nyholm, R. S. *J. Chem. Soc.* **1959**, 3997.

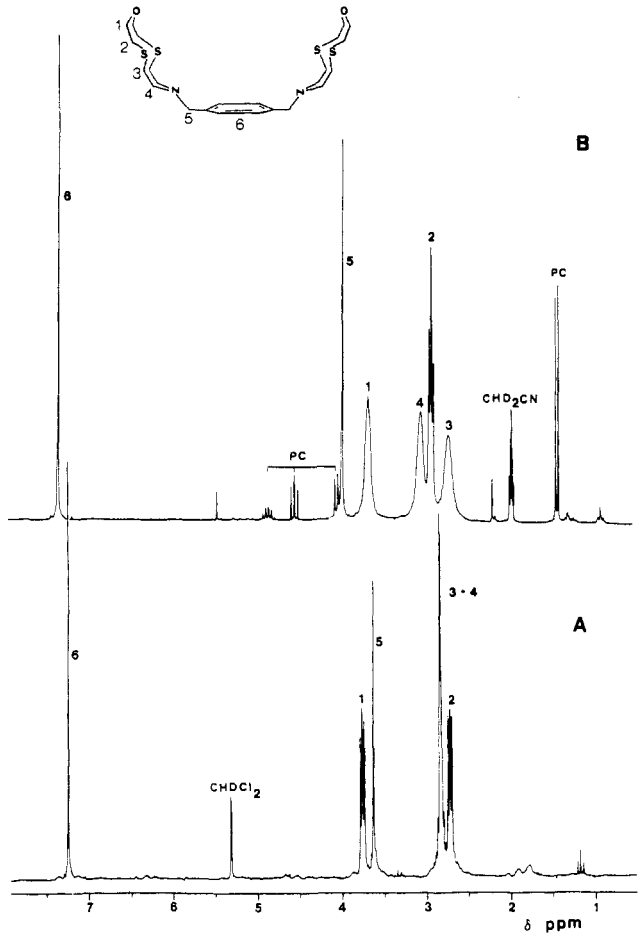



**Figure 2.** $^1H$ NMR spectra with assignments of (A) the binucleating ligand L in $CD_2Cl_2$ and (B) $[Cu_2L](BF_4)_2 \cdot 0.9PC$ in $CD_3CN$.

nomenon. Several remarks can be made concerning this study. First, in these donor solvents the coordination about each Cu(I) is uncertain. The binding of the $N_2S$ donor set would seem evident, but the ether oxygen (despite the slight shift of the protons 1) could be noncoordinating as has been found in other molecules of this type. However, in noncoordinating (or weakly coordinating) solvents these Cu(I) complexes react readily with $O_2$ whereas no reaction occurs if a coordinating solvent (or $PPh_3$, CO (see below)) is present. We suggest that the ether oxygen is thus either noncoordinating or very labile, and we thus favor the four-coordinate quasi-tetrahedral structure in solution shown in Figure 4. Second, the similarity between the spectra of the dinuclear $[Cu_2L]^{2+}$ and mononuclear $[CuL']^+$ complexes indicates that the local structures around each Cu(I) are without doubt identical and that little if any interaction occurs between copper(I) sites in $[Cu_2L]^{2+}$. Third, the variable-temperature spectra indicate a dynamic process is occurring that equilibrates pairs of ring protons. For example, the equilibration of outer (3a) and inner (3b) protons as well as (4a) with (4b) must take place for such spectral changes to be observed. This process occurs with an estimated barrier of ca. 13.8 kcal $mol^{-1}$. Such a behavior can only be explained if the Cu(I) ions have access to the *other face of the macrocycle* on the NMR time scale. Passage of the Cu(I) through the center of the monocycle would appear highly unlikely since the 12-membered ring is not sufficiently large to allow such a process and, further, would also necessitate the inversion at nitrogen in L, which is not possible while Cu(I) remains coordinated. We propose that, in these strongly coordinating solvents, rapid exchange occurs between ligand-coordinated Cu(I) and a solvated form (e.g. $[Cu(CH_3CN)_4]^+$) although the equilibrium must be overwhelmingly in favor of the ligated complex.

The evidence for the ready availability of a coordination site in solution is also supported by the facile formation of the bis(triphenylphosphine) adduct $[Cu_2(PPh_3)_2L]^{2+}$ (**5**) by the addition

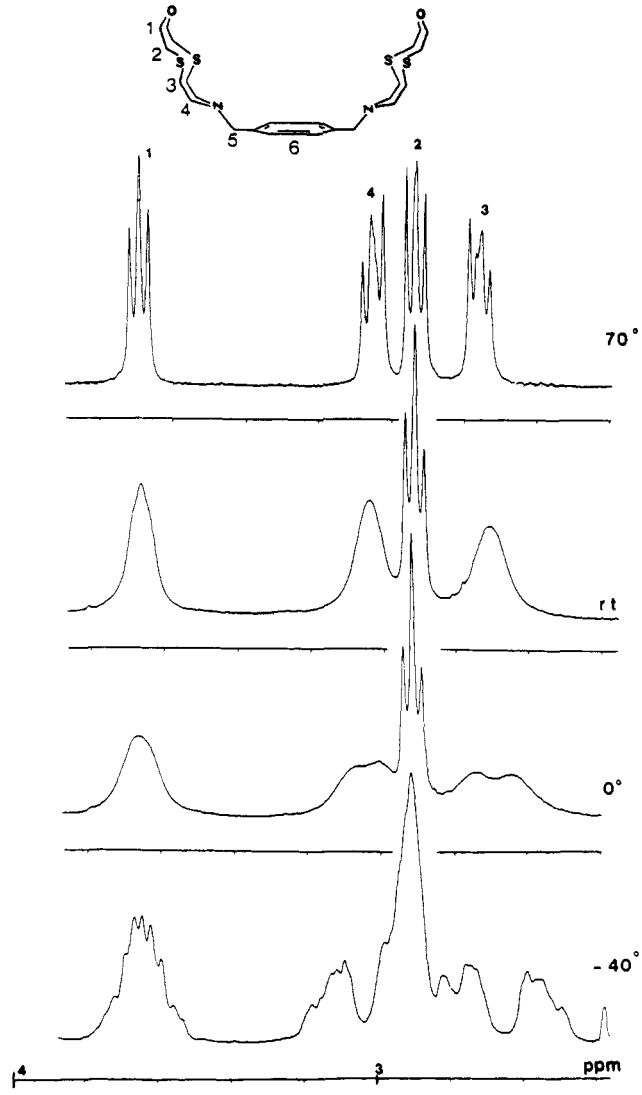



**Figure 3.** $^1H$ NMR spectra of $[Cu_2L](BF_4)_2 \cdot 0.9PC$ at different temperatures in $CD_3CN$.

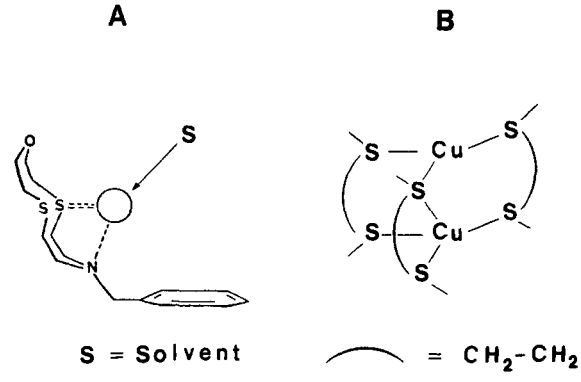



**Figure 4.** Proposed structures in solution of (A) $[Cu_2L]X_2$ and $[CuL']X$ (representation of one coordination site) and (B) $[Cu_2L'_3](X_2)$.

of 2 mol of $Ph_3P$ to **4** in acetonitrile. The $^{31}P$ NMR spectrum of this compound shows a singlet at $\delta(^{31}P) = 2.50$ (free $PPh_3$, $\delta(^{31}P) = -4.26$), indicating coordination to copper(I). Furthermore, in **5** the $^1H$ resonances of L again show broadening at room temperature except for the benzylic protons 5 and the aromatic protons 7, which are now shifted upfield, probably because of the influence of the phenyl groups of $PPh_3$.

The accessibility of the copper(I) centers to reaction is also demonstrated by the formation of carbonyl adducts of $[Cu_2L](BF_4)_2$. A suspension of **4** in degassed propylene carbonate at room temperature reacts rapidly with CO, as indicated by the fast

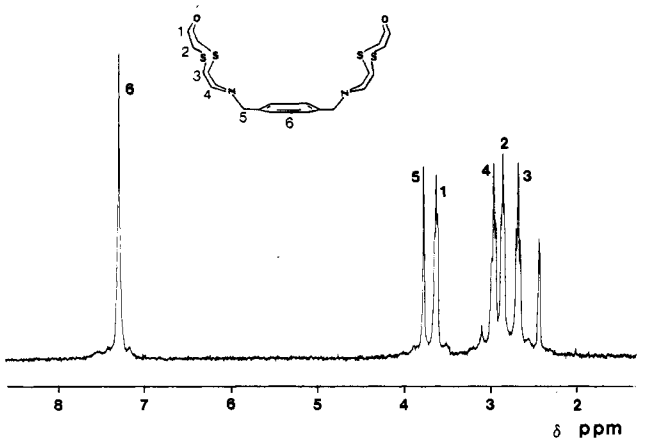



**Figure 5.** $^1H$ NMR spectrum of $[Cu_2L']X_2$ in $Me_2SO$-$d_6$.

dissolution of **4** upon exposure to carbon monoxide. Evidence for binding of CO is provided by the appearance of a IR band $\nu_{CO}$ at 2080 $cm^{-1}$, which is consistent with the formation of a terminal carbonyl adduct,[21] as well as of an additional electronic absorption at 260 nm ($\epsilon \approx 3800$ $M^{-1}$ $cm^{-1}$) in PC. Sweeping the solution with argon for $^1/_2$ h restores the initial spectra. By further CO/Ar cycles, the reversibility was also observed. Additional evidence of the formation of the adduct is given by polarography in PC.[22]

The $^1H$ and $^{13}C$ NMR spectra (Figure 5) of the complex $[Cu_2(L')_3]^{2+}$ show it to possess a highly symmetrical structure, and thus we propose the dimer structure in Figure 4, in which the two sulfur atoms of each of three L′ ligands serve to bridge two copper(I) sites. A symmetric arrangement of the L′ groups in which a threefold axis about the copper–copper axis is generated is consistent with the NMR data.

Finally the binuclear Cu(II) complex **2** shows a partially resolved contact shift spectrum and, in particular, the aromatic ligand protons occurring at $\delta$ 9.49 at 15 °C in $CD_3CN$; the other ligand resonances are, however, too broad to be reasonably assigned.

**(c) Electronic Spectra of the Cu(II) Complexes.** The electronic spectrum (Figure 6) of **1** (in $H_2O$ or propylene carbonate (PC)) shows absorptions at 670 ($\epsilon$ 1030), 390 (8630), 315 (4100) and 275 nm (sh). In the reflectance spectrum the low-energy band was identical other than the splitting into 660 nm with a shoulder at 585 nm. For **3**, absorptions were observed at similar energies except the molar extinction coefficients were approximately half of those found in **1**. This would indicate that no strong interaction is occurring between the Cu(II) ions in **1**. By comparison with other Cu(II) complexes[2] formed with thioether, nitrogen, or oxygen ligands, we would assign the relatively low-intensity absorption at ca. 670 nm as a d–d transition and the high-intensity band at 390 nm to a S → Cu(II) charge-transfer band.

The bridged species **2** shows a spectrum closely similar to that of **1** with absorptions at 685 (970), 585 (sh), 375 (8500), and 315 nm (2775) but has in addition a strong absorption at 447 nm (6360). The reflectance spectrum shows identical features, indicating that the solution structure is maintained in the solid state. The assignment of the 447-nm absorption is not clear, although one is at first tempted to associate this transition with the presence of the bridging OH group between the Cu(II) centers. However, absorptions typical of an O(OH) → Cu(II) CT transition have yet to be assigned with certainty for square-pyramidal or trigonal-bipyramidal geometries. Other complexes of this family containing a bridging ligand (e.g. imidazole) do not show this transition. At present we tentatively propose that (as for the 375-nm band) this absorption arises from a S → Cu(II) CT transition, the $S(\pi) \rightarrow d_{x^2-y^2}$ and $S(\sigma) \rightarrow d_{x^2-y^2}$ transitions occurring at slightly different energies.

The magnetic moment of **1** at 293 K was 1.85 $\mu_B$/Cu(II) in agreement with a pair of noninteracting Cu(II) ions. Further, the EPR spectrum of the solid showed a resonance at $g = 2.099$ (at 293 K) with no detectable $\Delta m = 2$ transition. In contrast, the room-temperature magnetic moment of **2** was found to be 0.48 $\mu_B$/Cu(II), indicating considerable antiferromagnetic coupling of the electron spins in the binuclear Cu(II) unit. In agreement with this observation the EPR spectrum of the solid presented a $\Delta m = 2$ transition at half-field, and a temperature-dependence study showed the singlet–triplet separation ($-2J$) to be ca. 850 $cm^{-1}$. The magnetic[7b] behavior of this complex has been reported, and a comparison with other bridged Cu(II) dimers will appear in a separate publication.

**(d) Ligand Protonation Studies by Potentiometric Methods.** In order to compare the relative basicities and behaviors of the two ligands L and L′, we have obtained their protonation constants by potentiometric methods. Because the ligands L and L′ are not appreciably soluble in water, we have studied the pH changes involved on treating the water-soluble protonated forms, $LH_2^{2+}$, $LH^+$, and $L'H^+$, with known quantities of LiOH. The protonation constants are thus expressed in the unusual way

$$LH_2^{2+} \rightleftharpoons LH^+ + H^+ \qquad \beta_{1:1} = \frac{[LH^+][H^+]}{[LH_2^{2+}]}$$

$$LH_2^{2+} \rightleftharpoons L + 2H^+ \qquad \beta_{1:2} = \frac{[L][H^+]^2}{[LH_2^{2+}]}$$

$$L'H^+ \rightleftharpoons L' + H^+ \qquad \beta'_{1:1} = \frac{[L'][H^+]}{[L'H^+]}$$

Details are found in the Experimental Section. Calculations were performed by a nonlinear least-squares method using the computer program SCOGS[23] and gave the following values (0.1 $LiNO_3$, 25 °C): $-\log \beta_{1:2} = 7.05 + 0.10$; $-\log \beta_{1:2} \geq 17$; $-\log \beta_{1:1} = 7.00 + 0.05$.

Note, however, that $\beta_{1:2}$ is an estimated value since L begins to precipitate at about pH 9, which precludes an accurate determination, but projects that the first protonating constant of L is greater than 10. This value is more than 3 $pK_a$ units greater than in L′. The origin of this marked effect would appear to lie in the potential chelate (or earmuff) behavior of L. Diamines in which an aquated proton (i.e. $H_3O^+$, $H_5O_2^+$) can interact with both nitrogen atoms via a bridging hydrogen-bonding interaction have generally widely separated first and second protonated constants; e.g. in 2,2′-bipyridine[24] these constants differ by 5 $pK$ units. Note, however, that in biphenyl-4,4′-diamine, where intramolecular bridging interactions cannot readily take place, the $pK_a$ values are only separated by ca. 1 $pK$ unit (4.95 and 3.85[24]). Thus, in contrast to L′, the flexibility of L allows an additional stabilizer of the order of 4 kcal $mol^{-1}$ by the formation of a hydrogen-bonding interaction between the first protonated nitrogen and the second nitrogen, certainly through water molecules.

**(e) Thermodynamics of Complexation of Cu(II).** In order to determine the nature of the Cu(II) species present under various conditions and their stability, a detailed thermodynamic study was undertaken in both water and PC using L and L′. The same conditions were applied as for the potentiometric study (see Experimental Section). The LETAGROP-SPEFO program was used to give the best fit of the electronic spectral data together with the stability constants for a given model.[25] With use of the HALTAFALL program[26] the concentration of each species can be de-

(21) Grzybowski, J. J.; Urbach, F. L. *Inorg. Chem.* **1980**, *19*, 2604.
(22) Unpublished results. Under a CO atmosphere, the anodic shift of the half-wave potential corresponding to the oxidation of the copper(I) dimer is 70 mV; such a behavior has already been observed and corresponds to a greater stabilization of copper(I). A second wave at −0.67 V, which disappears when the solution is flushed with argon, has been observed, but its origin has not been investigated any further.
(23) Sayce, I. G. *Talanta* **1968**, *15*, 1397.
(24) Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solutions"; Butterworths: London, 1965.
(25) Sillen, L. G.; Warnqvist, B. *Ark. Kemi.* **1969**, *31*, 377.
(26) Ingri, N.; Kakolowicz, W.; Sillen, L. G.; Warnqvist, B. *Talanta* **1967**, *14*, 1261.

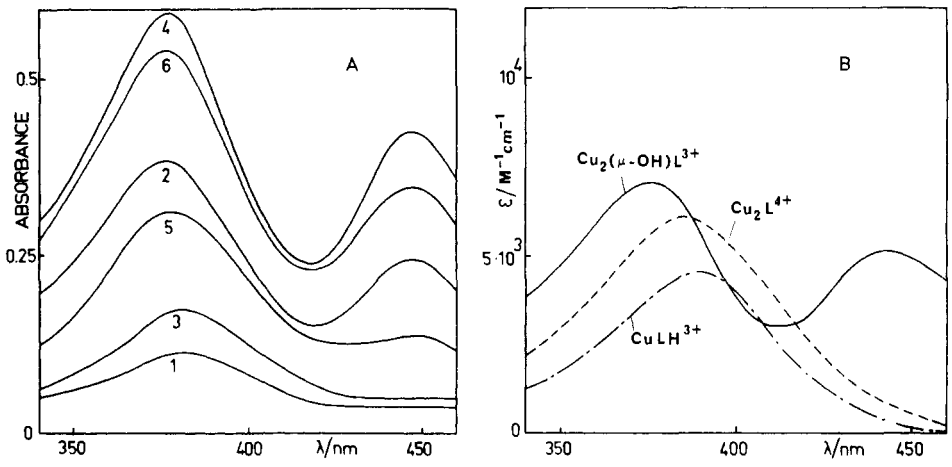



**Figure 6.** (A) Electronic spectra of Cu(II)/L/$H_2O$ at different concentrations and pH values (2-cm cells, 25 °C, 0.1 M $LiNO_3$): (1) $[Cu^{2+}] = 1.4 \times 10^{-4}$ M, $[L] = 8.8 \times 10^{-5}$ M, pH 5.22; (2) $[Cu^{2+}] = 1.4 \times 10^{-4}$ M, $[L] = 8.8 \times 10^{-5}$ M, pH 5.92; (3) $[Cu^{2+}] = 4.6 \times 10^{-4}$ M, $[L] = 8.8 \times 10^{-5}$ M, pH 4.92; (4) $[Cu^{2+}] = 4.6 \times 10^{-4}$ M, $[L] = 8.8 \times 10^{-5}$ M, pH 6.02; (5) $[Cu^{2+}] = 9.1 \times 10^{-4}$ M, $[L] = 8.6 \times 10^{-5}$ M, pH 4.94; (6) $[Cu^{2+}] = 9.1 \times 10^{-4}$ M, $[L] = 8.6 \times 10^{-5}$ M, pH 5.34. (B) Calculated absorbance spectra.

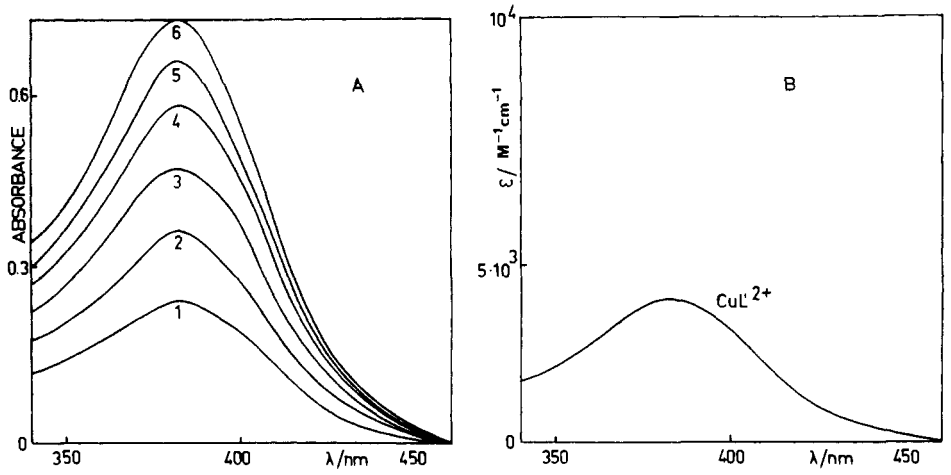



**Figure 7.** (A) Electronic spectra of Cu(II)/L'/$H_2O$ at different $Cu^{2+}$ concentrations (2-cm cells, 25 °C, 0.1 M $LiNO_3$, $[L'] = 1.69 \times 10^{-4}$ M, pH 5.95): (1) $4 \times 10^{-5}$ M; (2) $5.95 \times 10^{-5}$ M; (3) $7.93 \times 10^{-5}$ M; (4) $9.90 \times 10^{-5}$ M; (5) $1.18 \times 10^{-4}$ M; (6) $1.38 \times 10^{-4}$ M. (b) Calculated absorbance spectrum.

**Table I.** Complexation of Cu(II) by L and L' in $H_2O$[a]

| ligand | equil | constants | $\epsilon^*_{max}$, $M^{-1}$ $cm^{-1}$ |
|---|---|---|---|
| L | $Cu^{2+} + LH_2^{2+} \rightleftharpoons CuLH^{3+} + H^+$ | $\log K_1 = -2.0 \pm 0.1$ | $\epsilon_{390} = 4600$ |
| | $Cu^{2+} + CuLH^{3+} \rightleftharpoons Cu_2L^{4+} + H^+$ | $\log K_2 = -1.8$ | $\epsilon_{385} = 6200$ |
| | $Cu_2L^{4+} + OH^- \rightleftharpoons Cu_2(\mu\text{-}OH)L^{3+}$ | $\log K_3 = 9.2$ | $\epsilon_{375} = 7000$<br>$\epsilon_{445} = 5200$ |
| L' | $Cu^{2+} + L'H^+ \rightleftharpoons CuL'^{2+} + H^+$ | $\log K'_1 = -1.5 \pm 0.1$ | $\epsilon_{383} = 4100$ |

[a] Measurements were carried out in the range of concentration $10^{-5}$–$10^{-3}$ M for Cu(II) and the ligands, from pH 3 to 7 in 0.1 M $LiNO_3$ at 25 °C. Calculations were performed at the following wavelengths: 360, 370, 376, 380, 390, 400, 410, 420, 430, 440, 445, 450, 460, 470, 480 nm (L); 360, 370, 380, 383, 390, 400, 410, 420, 430 nm (L'). $\epsilon^*_{max}$ corresponds to the species formed in the written equilibrium.

termined. In Figures 6 and 7, experimental data in the 500–350-nm region at various concentrations and pH values for both L and L' are presented along with the calculated data. The best model given by calculation involves the equilibria presented in Table I. The ligand L forms, depending on the pH, the three complexes $[CuLH]^{3+}$, $[Cu_2L]^{4+}$, and $[Cu_2(\mu\text{-}OH)L]^{3+}$. Only the $[CuL']^{2+}$ complex is observed for L', a dimer form of the type $[Cu_2(\mu\text{-}OH)L'_2]^{3+}$ not being detected. This contrasts with the high stability of $[Cu_2(\mu\text{-}OH)L]^{3+}$ ($K_3 = 1.6 \times 10^9$ $M^{-1}$), which is evident from the formation curves represented in Figure 8. These stability measurements can be compared with those made

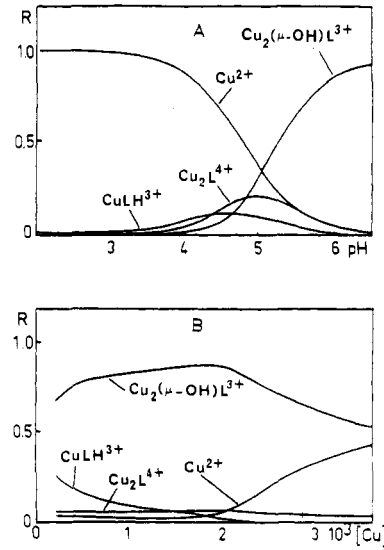



**Figure 8.** Formation curves in aqueous solutions for the cupric species with L ($R = [Cu]_{complexed}/[Cu]_{anal.}$): (A) as a function of pH with $[L]_{anal.} = 10^{-3}$ M and $[Cu]_{anal.} = 2 \times 10^{-3}$ M; (B) as a function of $[Cu]_{anal.}$ with $[L]_{anal.} = 10^{-3}$ M and pH 6.

on the known mononuclear complex $[Cu(tet\text{-}b)OH]^+$ (where tet-b = macrocyclic tetraamine), which has in water a $K$ value of $5 \times 10^2$ $M^{-1}$.[27] Hence, the conformational flexibility of L allows the

**Table II.** Pseudo-First-Order Rate Constant of the Decomplexation Reaction of $[CuL']^{2+}$ by $H^+$ [a]

| $10^3[H^+]_0$, M | $k'_{obsd}$, $s^{-1}$ | $10^3[H^+]_0$, M | $k'_{obsd}$, $s^{-1}$ |
|---|---|---|---|
| 2 | 0.065 ± 0.003 | 8 | 0.067 ± 0.002 |
| 2 | 0.067 ± 0.002 | 20 | 0.070 ± 0.003 |
| 4 | 0.070 ± 0.003 | 20 | 0.069 ± 0.002 |
| 4 | 0.070 ± 0.003 | 40 | 0.070 ± 0.004 |
| 8 | 0.068 ± 0.002 | 40 | 0.074 ± 0.005 |

[a] $[H^+]_0$ is the initial concentration. $[CuL'^{2+}]_0 = 0.56 \times 10^{-4}$ M.

formation of a bridged hydroxy species of high stability at a relatively low pH value. The driving force for the activation of small molecules (e.g. $H_2O$, imidazole) by these binuclear complexes is thus not only the polarization of such molecules by interaction with both Cu(II) ions (kinetic effect) but also the *thermodynamic stabilization of the conjugate base* ($OH^-$, imidazolate anion) by its *double coordination to the binuclear unit.* We shall discuss the formation of a binuclear bridged imidazolate complex of Cu(II) that further illustrates these efects in a later paper.

Studies were also carried out in propylene carbonate, and the spectra of copper(II) in the presence of L or L′ exhibit the same absorptions as in water. Despite intensive drying of the PC, residual water ($\sim 10^{-2}$ M) is involved in the equilibria and no reasonable model could be computed from the data.

**(f) Kinetics of Complexation of Cu(II).** A study of the kinetics of acid-decomplexation reactions was carried out using UV/visible spectral changes. The decomplexation of $Cu_2L^{4+}$ was followed at 383 nm and of $Cu_2(\mu\text{-OH})L^{3+}$ at 460 nm while $CuL'^{2+}$ was studied at 385 nm. The acidification of the solutions of these complexes gives rise to the overall equations

$$CuL'^{2+} + H^+ \rightarrow Cu^{2+} + L'H^+$$

$$Cu_2(\mu\text{-OH})L^{3+} + 3H^+ \rightarrow 2Cu^{2+} + LH_2^{2+} + H_2O$$

The reactions were studied under pseudo-first-order conditions by using an excess of $H^+$.

**(i) Decomplexation of $CuL'^{2+}$.** The kinetic data are consistent with a rate law of the form

$$v = k'_{obsd}[CuL'^{2+}]$$

$k_{obsd}$ was found to be independent of the $H^+$ concentration (from $2 \times 10^{-3}$ to $4 \times 10^{-3}$ M) as shown in Table II. The most reasonable mechanism would be a dissociative one, according to the scheme

$$CuL'^{2+} \xrightarrow{k'_D} Cu^{2+} + L'$$

$$k'_D = 0.069 \pm 0.004 \text{ s}^{-1}$$

$$L' + H^+ \xrightarrow{\text{fast}} HL'^+$$

**(ii) Decomplexation of $Cu_2(\mu\text{-OH})L^{3+}$.** This study was carried out in the same range of concentration of $H^+$ as above. The system involves two steps. The first, which is fast, corresponds to the disappearance of the band at 447 nm and can be interpreted by the protonation of the bridging $OH^-$ to give $H_2O$ and $Cu_2L^{4+}$. The second step proceeds with a rate slow enough to be followed at 383 nm, independently of the rapid formation of $Cu_2L^{4+}$. It is obvious from Table III that the two reactions are consistent with the experimental laws

$$-d[Cu_2(\mu\text{-OH})L^{3+}]/dt = k_{obsd}[Cu_2(\mu\text{-OH})L^{3+}]$$

$$k_{obsd} = k_H[H^+] \qquad k_H = 2500 \pm 200 \text{ M}^{-1} \text{ s}^{-1}$$

$$-d[Cu_2L^{4+}]/dt = k_{obsd}[Cu_2L^{4+}]$$

$$k_{obsd} = k_D = 0.140 \pm 0.008 \text{ s}^{-1}$$

(27) Liang, B. F.; Margerum, D. W.; Chung, C. S. *Inorg. Chem.* **1979**, *18*, 2001.

**Table III.** Pseudo-First-Order Rate Constants of the Decomplexation Reaction of $[Cu_2(\mu\text{-OH})L]^{3+}$ and $[Cu_2L]^{4+}$ by $H^+$ [a]

| | $k_{obsd}$, $s^{-1}$ | |
|---|---|---|
| $10^3[H^+]_0$, M | $[Cu_2(\mu\text{-OH})L]^{3+}$ | $[Cu_2L]^{4+}$ |
| 2.5 | 9.2 ± 0.3 | 0.135 ± 0.007 |
| 2.5 | 8.8 ± 0.3 | 0.139 ± 0.008 |
| 5 | 15.6 ± 1.0 | 0.135 ± 0.009 |
| 5 | 14.9 ± 0.9 | 0.140 ± 0.007 |
| 10 | 27.6 ± 2.1 | 0.142 ± 0.008 |
| 10 | 29.1 ± 2.4 | 0.144 ± 0.007 |
| 25 | 72.3 ± 3.3 | 0.140 ± 0.009 |
| 25 | 69.8 ± 3.0 | 0.139 ± 0.009 |
| 40 | 106 ± 13 | 0.141 ± 0.007 |
| 40 | 112 ± 12 | 0.140 ± 0.006 |

[a] $[H^+]_0$ is the initial concentration. $[Cu_2(\mu\text{-OH})L^{3+}]_0 = 0.5 \times 10^{-3}$ M.

The experimental data are consistent with the proposed mechanism

$$Cu_2(\mu\text{-OH})L^{3+} + H^+ \overset{k_H}{\rightleftharpoons} Cu_2L^{4+} + H_2O \quad (1)$$

$$Cu_2L^{4+} \overset{\text{slow}}{\rightleftharpoons} CuL^{2+} + Cu^{2+} \quad (2)$$

$$CuL^{2+} + H^+ \overset{\text{very fast}}{\rightleftharpoons} CuLH^{3+} \quad (3)$$

$$CuLH^{3+} \overset{\text{slow}}{\rightleftharpoons} Cu^{2+} + LH^+ \quad (4)$$

$$LH^+ + H^+ \overset{\text{very fast}}{\rightleftharpoons} LH_2^{2+} \quad (5)$$

The rate-determining step would thus involve either reaction 2 or 4, which proceeds with a rate of the same order of magnitude as the reaction of decomplexation of $CuL'^{2+}$ ($k_D = 2k'_D$). This confirms the independent nature of the coordination sites in $Cu_2L^{4+}$.

By contrast, the protonation of the bridging hydroxo ligand is exceptionally fast despite its overall thermodynamic stability. Hence, the flexibility of this ligand allows not only the extremely rapid complexation and stabilization of the $OH^-$ moiety but also its rapid decomplexation under the appropriate conditions.

## Conclusions

We have shown in this paper that incorporation of two copper sites in a conformationally flexible binucleating ligand imparts certain interesting properties. The binuclear effect allows the activation of small molecules and stabilization of the conjugate anions in a bridging mode (e.g. in $[Cu^{II}(\mu\text{-OH})Cu^{II}]^{3+}$). The flexibility of the ligand permits such reactions to be kinetically rapid and reversible. We will discuss these points in later papers and their possible significance in the function of certain metalloenzymes.

**Acknowledgment.** We thank Prof. J. E. Bulkowski and Dr. P. L. Burk for their contribution in the initial stage of this work.

**Registry No.** **1**, 76706-00-8; **2**, 77257-86-4; **3**, 99727-48-7; **4a**, 95246-12-1; **4b**, 99781-75-6; **4c**, 99727-49-8; **4d**, 99727-50-1; **5**, 99727-52-3; **6** (X = $BF_4$), 99748-36-4; **6** (X = $ClO_4$), 99727-54-5; **7** (X = $BF_4$), 99727-56-7; **7** (X = $ClO_4$), 99727-57-8; L, 79503-03-0; L′, 99727-59-0; L′·HCl, 99727-60-3; $H_2N(CH_2CH_2Br)_2Br$, 43204-63-3; $O(CH_2CH_2SNa)_2$, 78907-71-8; $HN(CH_2CH_2OH)_2$, 111-42-2; $TsN(CH_2CH_2OTs)_2$, 16695-22-0; $C_6H_4$-1,4-$(COCl)_2$, 100-20-9; $[Cu(CH_3CN)_4](BF_4)$, 15418-29-8; *N*-(1-oxa-4,10-dithia-7-azacyclododec-7-yl)-*p*-methylbenzenesulfonamide, 99727-58-9; 1-oxa-4,10-dithia-7-azacyclododecane, 24918-63-6.