cloalkadienes (1) were prepared according to the following procedure. To a suspension of sodium dispersion (0.45 g-atom) and trimethylchlorosilane (0.5 mol) in xylene (300 mL), dimethyl decanedioate (0.1 mol) in xylene (30 mL) was added dropwise with vigorous stirring over 3 h at 40–50 °C. Then the mixture was heated at 80 °C for 3 h and allowed to stand overnight at room temperature. After the reaction mixture was filtered, the filtrate was distilled in vacuo. Removal of 1,2-bis(trimethylsilyloxy)cyclodecene by Kugelrohr distillation left a viscous liquid, which was slowly solidified and recrystallized from ether to give pure **1b**, mp 89–90 °C (lit.[2a] mp 90–90.5 °C), in 47% yield. Compounds **1a**, **1c**, and **1d** were separated from 1,2-bis(trimethylsilyloxy)cyclononene, 1,2-bis(trimethylsilyloxy)cyclododecene, and 1,2-bis(trimethysilyloxy)cyclotetradecene, respectively, by Kugelrohr distillation and subjected to the subsequent cyclopropanation without further purification.

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(6) Calculated relative intensity: 425 (100), 426 (24.39), 427 (48.07), 428 (11.06).

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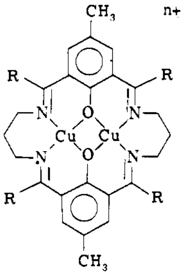
Binuclear Complexes of Macrocyclic Ligands. A Mixed-Valence Copper(II)-Copper(I) Complex which Exhibits Unusual Temperature-Dependent Behavior

Sir:

Macrocyclic ligands can provide transition metals with unusual ligand environments and consequent novel chemical properties: high and low oxidation states are often stabilized;[1] ligand lability is lessened by the chelating effect;[2] several metal atoms may be held in close steric proximity within the same molecule.[3] Capitalizing on these properties of macrocyclic ligands we are studying the behavior of binuclear copper complexes as models for copper-containing proteins.[4] Herein we report preliminary observations on two mixed-valence, copper(II)-copper(I), macrocyclic ligand complexes, one of which exhibited unusual temperature-dependent behavior.

Condensation of 5-methyl-2-hydroxyisophthalaldehyde with 1,3-diaminopropane in the presence of $Cu(ClO_4)_2 \cdot 6H_2O$ yielded the binuclear copper(II) complex, $Cu^{II}Cu^{II}L$, **1**.[5,6] We



1, Cu(II)-Cu(II), n = 2, R = H

2, Cu(II)-Cu(I), n = 1, R = H

3, Cu(II)-Cu(I)(CO), n = 1, R = H

4, Cu(II)-Cu(I), n = 1, R = CH_3

have not been successful in reducing the complex with chemical reducing agents. Cyclic voltammetry in DMF,[7] however, revealed two quasi-reversible reduction waves ($E_1{}^f \simeq -0.52$ V, $E_2{}^f \simeq -0.91$ V, $n_1 = n_2 = 1.0 \pm 0.1$) by CPE).[8] Electrolysis of green solutions of **1** (−0.7 V, CH_3CN/N_2, $n = 1.0 \pm 0.1$) resulted in a dark brown solution. A nearly black solid, corresponding to the formula $Cu^{II}Cu^{I}L(ClO_4)$, **2**,[6] was precipitated from solution by the addition of Et_2O. Saturation of the electrolysis solution with CO followed by addition of Et_2O led to precipitation of a CO adduct, $Cu^{II}Cu^{I}L(CO)ClO_4$, **3**,[6,10] (ν_{CO} 2065 cm^{-1}), presumably containing five-coordinate copper(I).

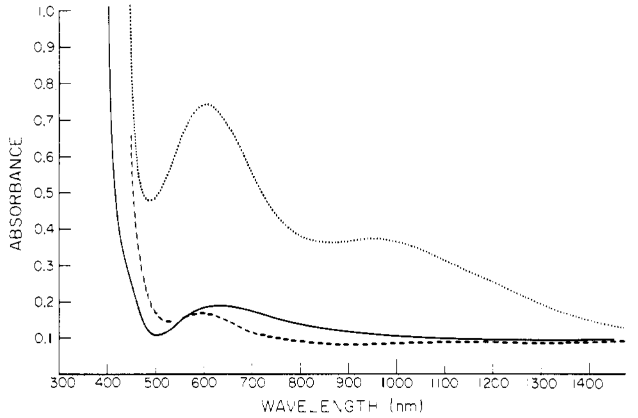


Figure 1. Electronic absorption spectra in methanol of $Cu^{II}{}_2L(ClO_4)_2(H_2O)_2$, **1** (—); $Cu^{II}Cu^{I}LClO_4$, **2** (· · · ·) under helium; $Cu^{II}Cu^{I}(CO)LClO_4$, **3** (- - -) under carbon monoxide. $[Cu^{II}{}_2] = 1.15 \times 10^{-3}$ M; $[Cu^{II}Cu^{I}] = [Cu^{II}Cu^{I}(CO)] = 1.10 \times 10^{-3}$ M.

Representative electronic absorption spectra of **1**, **2**, and **3** are shown in Figure 1. All three complexes exhibited intense absorptions in the 350–400-nm region (ε 10 000–15 000, presumably ligand absorption) and a weaker band at ~600 nm. Since only the 350–400-nm band was observed in the zinc complex $Zn^{II}Zn^{II}L(ClO_4)_2(H_2O)_2$,[6] we tentatively assign the 600-nm absorptions in **1**, **3**, and **2** (in part) to a ligand field copper(II) transition.[12] Most notable in the spectra was a broad band in the near infrared seen only for **2.** We tentatively assign this as an intervalence-transfer transtion (IT) (copper(II)-copper(I) → copper(I)-copper(II)*).[13] The position of the IT band maximum appeared to be dependent on the solvent donor properties. In noncoordinating CH_2Cl_2 the band was at ~1200 nm (ε ≃80), while in weakly coordinating CH_3OH, $(CH_3)_2CO$, and DMF the band shifted to ~900 nm. In CH_3CN, which appears capable of forming five-coordinate copper(I) adducts,[9-11] no IT band was observed.

The addition of CO to $Cu^{II}Cu^{I}L$, **2**, to give the carbonyl adduct, $Cu^{II}Cu^{I}L(CO)$, **3**, was essentially complete (in CH_3OH, $(CH_3)_2CO$, DMF, CH_3CN, CH_2Cl_2) as monitored by electronic absorption spectroscopy and cyclic voltammetry.[14] For example, addition of CO to bluish green solutions of **2** (CH_3OH) led to yellow solutions with the electronic spectra of **3** (Figure 1). The lack of an observable IT band for **3** appears consistent with the spectra of **2** in donor solvents; i.e., CO adduct formation may shift the IT band to high energies where it is masked by ligand absorption.

Solution EPR spectra for $Cu^{II}Cu^{I}L$, **2** (Figure 2), consisted of seven lines, consistent with interaction of the odd electron with both copper centers ($I = 3/2$). Internally consistent hyperfine splittings in both solvents imply the presence of only a single EPR active species. In contrast frozen solutions at liquid-nitrogen temperature exhibited four-line anisotropic spectra (CH_2Cl_2 or CH_3CN).[15] Similarly, addition of CO to solutions of **2** resulted in a solution of **3** (by electronic spectra) and an EPR spectrum having only four lines (25 °C, CH_2Cl_2). These four-line spectra, whether from frozen solutions of **2** or solutions of **3** at 25 °C, are consistent with localization of the odd electron on a single copper center, at least on the relatively slow EPR time scale (10^{-8}-10^{-4} s).[16]

Possible explanations for the temperature-dependent behavior of **2** include (1) axial ligation by ClO_4^- or solvent (CH_3CN or CH_2Cl_2) at low temperature leads to an asymmetric complex comparable with the carbonyl adduct, **3**; or (2) macrocyclic ligand conformational changes which accompany electron exchange (possibly distorted tetrahedral for copper(I)

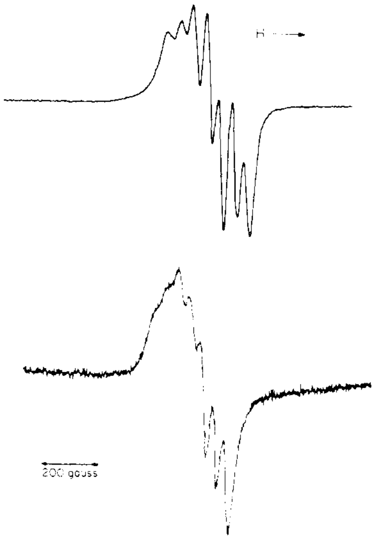


Figure 2. Solution X-band EPR spectra (25 °C) of $Cu^{II}Cu^{I}L(ClO_4)$, **2**, in CH_2Cl_2 (top) and CH_3CN (bottom).

to distorted square planar for copper(II)) become more difficult in frozen solutions resulting in a "locked-in" configuration on the EPR time scale.[16] The latter explanation is especially attractive for CH_2Cl_2 solutions of **2** in which, presumably, only ClO_4^- and CH_2Cl_2 are available for axial ligation.

These EPR results are in contrast to those recently reported by Addison on a similar macrocyclic copper(II)-copper(I) complex, **4** (R = CH_3), which exhibits four-line EPR spectra even at room temperature in CH_3CN.[17] In this case methyl substitution probably alters the conformational properties of the macrocycle sufficiently to inhibit thermal electron transfer on the EPR time scale at temperatures where it occurs with **2.**

It should be noted that several cobalt(III)-cobalt(II) complexes of this macrocycle (R = H) have been prepared and characterized crystallographically, although their mixed-valence spectral properties were not discussed.[18]

Five coordination for copper(I) is most unusual. That **2** exhibited an IT band is good evidence for the presence of copper(I), as opposed to a copper(II) radical anion. Since the $Cu^{II}Cu^{II}L$ complex, **1,** does not react with CO, then the CO adduct, $Cu^{II}Cu^{I}L(CO)$, **3,** if five-coordinate as is expected, must also be regarded as containing copper(I) with a most unusual coordination number.

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Stereochemistry of the S_N2' Reaction of an Acyclic Allylic Chloride with a Secondary Amine

Sir:

The S_N2' reaction (bimolecular nucleophilic substitution with allylic rearrangement) has been of synthetic and mechanistic interest for years.[1] Since the first reported example,[2] numerous instances of the process have been documented. Bordwell[1a,3] has argued that the concerted mechanism is incorrect; rather, all of these reactions proceed via an ion-pair intermediate of the type postulated by Sneen[4] for S_N reactions in general.

Regardless of the precise timing of the bond-making and bond-breaking steps, one can still inquire into the stereochemistry of the reaction. Most theoretical analyses have led to a predicted preference for syn attack[5,7] (in which the nucleophile and leaving group are on the same face of the allylic system), while allowing the possibility of anti stereochemistry for certain combinations of entering and leaving groups.[7c,e]

Until this year, the definitive experimental investigation of the stereochemistry was that of Stork and White[8] who showed that *trans*-6-alkyl-2-cyclohexen-1-yl 2,6-dichlorobenzoates underwent exclusive syn attack by piperidine and malonate. More recently, Stork and Kreft[9] reinvestigated this system (and the related mesitoate esters of the cis and trans isomers) and demonstrated that the stereochemistry could vary from predominantly syn to largely anti as the nucleophile was changed. One can argue, however, that a cyclohexenyl system has certain built-in conformational biases which force syn attack, independent of any stereoelectronic requirements of the S_N2' reaction.[10] An acyclic case, free of such complications, has been reported by Stork and Kreft[13a] who found that internal nucleophilic attack by a thiolate anion occurred primarily anti, although a closely related intramolecular process involving carbanionic attack proceeded syn.[13b] The only other stereochemical studies are those involving metal hydrides or organometallic reagents with allylic systems;[14] the outcome (a nearly random blend of syn and anti) and the doubtful relevance of such reactions to a truly nucleophilic process render these experiments of little value in the present context. We now report that the intermolecular S_N2' reaction in an unbiased acyclic case proceeds with syn stereospecificity.

The substrate selected for this study, (*R*)-(−)-3-chloro-(*Z*)-1-butene-*1-d* (**1**), is merely an isotopic variant of α-methylallyl chloride, the compound used by Young and coworkers[2,6,15] to establish the scope of the S_N2' reaction. *dl*-1-Butyn-3-ol (**2**) was reduced to *dl*-1-buten-3-ol-(*Z*)-*1-d* by $LiAlH_4$/THF followed by D_2O.[16] Resolution with brucine via