

Donor-Set-Induced Coordination Sphere and Oxidation-State Switching in the Copper Complexes of O₂S₂X (X = S, O and NH) Macrocycles

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Reaction of the O₂S₂X-macrocycles (**L**¹, X = S; **L**², X = NH; and **L**³, X = O) with Cu(ClO₄)₂·6H₂O affords 1:1 (M/L) square-pyramidal Cu(II) complexes when X = S and NH but yields a rare 1:2 sandwich-type tetrahedral Cu(I) complex when X = O; the X-ray structures of all three complexes are reported. Substitution of O for S or NH in the ligand structure thus results in a donor-set-induced II/I oxidation state change of the copper, and this is accompanied by a square-pyramidal to tetrahedral topological change in the solid state. Spectrophotometric titration data (including Job plots) indicate that similar behavior occurs in acetonitrile. In further experiments aimed at investigating the generality of the above redox behavior, it was shown that the 16- and 18-membered analogs of the 17-membered **L**³ also induce a similar II/I redox change in acetonitrile. It was demonstrated for **L**³ that the above-induced Cu(II/I) change is also maintained when the reaction solvent is changed from acetonitrile to methanol or ethanol.

Introduction

The relation between metal oxidation state, the geometry of the metal center, and the nature of the coordination sphere has always been a matter of fundamental importance to coordination, bioinorganic, and metallosupramolecular chemistry.¹ Because of steric constraints arising from their cyclic nature, macrocyclic ligand systems have frequently been employed for probing structure/function relationships

of this type.² While homoleptic macrocycles have commonly been used in such studies, the introduction of heterodonor atoms has frequently led to major changes in the metal binding ability, redox behavior, and complex geometry adopted.³ In an early study, Addison et al.⁴ reported Cu(I) and Cu(II) complexes of N₂S₂ macrocycles which showed a change of oxidation state with a change in ligand flexibility and ring size: the 15-membered ring formed a square-planar Cu(II) complex, while the 16-membered ring analog gave a pseudo-tetrahedral Cu(I) species. Subsequent work by other groups⁵ also confirmed that larger or more flexible S-containing macrocyclic rings capable of adopting a tetrahedral geometry about the central copper favor stabilization of the Cu(I) state. Other isolated reports of the spontaneous generation of Cu(I) complexes from Cu(II) starting reagents in the presence of S-containing ligands have also appeared.^{4,5a,6}

We have recently reported that variation of the X donor in O₂S₂X macrocycles (Chart 1; **L**¹, X = S; **L**², X = NH; **L**³,

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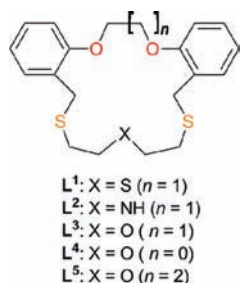
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Chart 1. O₂S₂X (X = S, O, and NH) Macrocycles

X = O) triggers marked changes in the coordination geometries of the corresponding Ag(I) complexes.^{3a} Clearly, such behavior reflects the difference in hardness, polarizability, and affinity toward Ag(I) of the different X donors. In view of this, it was of interest to explore the possible related behavior of these ligands toward copper, which in its +1 state also has a d¹⁰ electronic configuration. The results of such an investigation are now reported.

Experimental Section

General. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. Mass spectra were obtained on a JEOL JMS-700 spectrometer. The FT-IR spectra were measured with a Shimadzu FT-IR 8100 spectrometer. The elemental analyses were carried out on a LECO CHNS-932 elemental analyzer.

Preparation of 1, [Cu(L¹)(H₂O)(ClO₄)]ClO₄. Layering of an acetone solution (1 mL) of Cu(ClO₄)₂·6H₂O (47.0 mg, 0.127 mmol) onto an equal amount of L¹ (50.0 mg, 0.127 mmol) in dichloromethane (1 mL) gave dark green single crystals of **1** suitable for X-ray crystallography. Mp: 134–136 °C. IR (KBr pellet): 3064, 2977, 2919, 1595, 1491, 1451, 1244, 1087(ClO₄⁻), 1061sh (ClO₄⁻), 940, 753 cm⁻¹. Anal. Calcd for [C₂₀H₂₆Cl₂CuO₁₁S₃]: C, 36.67; H, 3.69; S, 14.69. Found: C, 36.20; H, 4.02; S, 14.21%. Mass spectrum *m/z* (FAB): 553.97 [Cu(L¹)(ClO₄)]⁺.

Preparation of 2, [Cu(L²)(H₂O)(ClO₄)]ClO₄·CH₃COCH₃. Layering of an acetone solution (1 mL) of Cu(ClO₄)₂·6H₂O (47.0 mg, 0.127 mmol) onto an equal amount of L² (50.0 mg, 0.133 mmol) in dichloromethane (1 mL) gave dark green single crystals of **2** suitable for X-ray crystallography. Mp: 134–136 °C. IR (KBr pellet): 3433br (H₂O), 3204 (NH), 2992, 2934, 2881, 1701, 1599, 1494, 1454, 1420, 1365, 1294, 1246, 1195, 1120sh (ClO₄⁻), 1105 (ClO₄⁻), 945, 757 cm⁻¹. Anal. Calcd for [C₂₃H₃₃Cl₂CuNO₁₂S₂]: C, 37.65; H, 3.95; N, 2.20; S, 10.05. Found: C, 37.77; H, 4.43; N, 1.79; S, 9.61%. Mass spectrum *m/z* (FAB): 537.01 [Cu(L²)(ClO₄)]⁺.

Preparation of 3, [Cu(L³)₂](ClO₄)₂·CH₃COCH₃. Cu(ClO₄)₂·6H₂O (49.0 mg, 0.133 mmol) in acetone (2 mL) was added to a solution of L³ (50.0 mg, 0.133 mmol) in dichloromethane (2 mL). After about 5 min of stirring at room temperature, the green reaction mixture became colorless. Bright-yellow single crystals suitable for X-ray crystallography were prepared by the slow evaporation of the yellow solution. Mp: 127–130 °C. IR (KBr pellet): 2922, 2851, 1592 (C=O), 1490, 1448, 1289, 1241, 1113 (ClO₄⁻), 1062, 946, 753 cm⁻¹. Anal. Calcd for [C₄₃H₅₄Cl₂CuO₁₁S₄]: C, 52.44; H, 5.28; S, 14.00. Found: C, 52.56; H, 5.72; S, 13.77%. Mass spectrum *m/z* (FAB): 815.16 [Cu(L³)₂]⁺.

Cyclic Voltammetry. Cyclic voltammograms were obtained using 1.0 mmol of the complexes in CH₃CN or CH₂Cl₂. The supporting electrolyte was 0.1 M Bu₄NClO₄; a platinum working electrode and a sodium saturated calomel reference electrode were employed, with a scan rate of 10 mV s⁻¹.

UV-Vis Titrations. UV-vis spectra were obtained using a SCINCO S-3150 spectrophotometer. The stock solution of

Cu(ClO₄)₂·6H₂O (0.01 M) in acetonitrile was added incrementally using an automatic pipet (0–20 μL) to L¹–L⁵ (3.0 × 10⁻⁴ M) in acetonitrile (3 mL) in a 1 cm quartz cell.

X-Ray Crystallographic Analysis. Crystal Data for 1 and 2. The diffraction data were measured at 100 K with synchrotron radiation [λ = 0.85000 (1) and 0.75000 (2) Å] on a 6BX Bruker Proteum 300 CCD detector with a platinum-coated double-crystal monochromator at the Pohang Accelerator Laboratory, Korea. The HKL2000 (version 0.98.694)⁷ software package was used for data collection, cell refinement, reduction, and absorption correction. Collected data were corrected for absorbance using SADABS based upon Laue symmetry using equivalent reflections. Table 1 provides crystal data for **1–3**, and Tables 2–4 provide selected bond lengths and angles for **1–3**, respectively.

Crystal Data for 3. The diffraction data were measured at 173 K on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo K α radiation (λ = 0.71073 Å). The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 45 collected frames) using the SMART program. The intensity data were processed using the Saint Plus program. All of the calculations for the structure determination were carried out using the SHELXTL package (version 6.22).⁸ Absorption corrections were applied using XPREP and SADABS.⁹

Results and Discussion

A comparative study of the interaction of Cu(II) with the 16- to 18-membered macrocycles L¹–L⁵ has been carried out. Each of these O₂S₂X ligands (X = S, NH, or O) was prepared as described previously by us.¹⁰

Copper(II) Complexes 1 and 2. The reaction of Cu(ClO₄)₂·6H₂O with one equivalent of L¹ or L² in CH₂Cl₂/acetone yielded dark-green crystals in each case with the 1:1 (M/L) stoichiometries [Cu(L¹)(H₂O)](ClO₄)₂·acetone (**1**) and [Cu(L²)(H₂O)(ClO₄)]ClO₄ (**2**) (see Scheme 1). Similar cation geometries are present in each case. Cu(II) is respectively bound to the S₃ donor set of L¹ and the S₂N donor set of L², with each coordination sphere being completed by one O atom from a water ligand and one from a monodentate perchlorate ion. In each complex, the Cu(II) lies inside the macrocyclic cavity but is displaced toward the bound S₂X donor set (Figures 1 and 2).

The coordination geometry of both complexes is best described as distorted square-pyramidal, with the –S–X–S– donor string from the macrocyclic ligand and the water oxygen occupying the basal plane in each structure. The Cu(II)-to-sulfur and -to-nitrogen bond lengths in each complex are unremarkable.¹¹ The perchlorate ion in each case is loosely axially bound [Cu1–O3 = 2.757 Å for **1** and 2.568 Å for **2**]. The Cu(II) ions are positioned 0.279 and 0.177 Å above the respective basal least-squares donor planes. Distortion from a regular square pyramid

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Table 1. Crystal and Experimental Data for 1–3

	1	2	3
formula	C ₂₀ H ₂₆ Cl ₂ CuO ₁₁ S ₃	C ₂₃ H ₃₃ Cl ₂ CuNO ₁₂ S ₂	C ₄₃ H ₅₄ ClCuO ₁₁ S ₄
formula weight	673.03	714.06	974.09
temperature (K)	100(2)	100(2)	173(2)
crystal system	orthorhombic	monoclinic	monoclinic
space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
Z	8	4	4
a (Å)	10.314(2)	18.353(4)	10.880(4)
b (Å)	15.819(3)	9.985(2)	17.347(6)
c (Å)	30.975(6)	16.607(3)	24.358(9)
β (deg)	90	104.16(3)	97.291(1)
V (Å ³)	5053.8(2)	2950.9(1)	4559.8(3)
D _x (g/cm ³)	1.769	1.607	1.419
2θ _{max}	56	52	55
R	0.0594	0.0712	0.0523
wR	0.1664	0.1962	0.1091
GOF	1.108	1.056	1.044
data/restraints/params	3472/0/329	4781/0/381	10415/0/541
abs correction	none	none	empirical SADABS
diffractometer	6BX Bruker Proteum 300	6BX Bruker Proteum 300	Bruker SMART CCD system
structure determination	SHELXTL	SHELXTL	SHELXTL
refinement	full-matrix	full-matrix	full-matrix

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 1

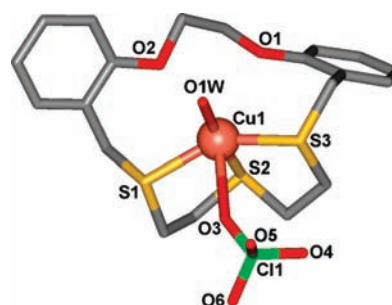
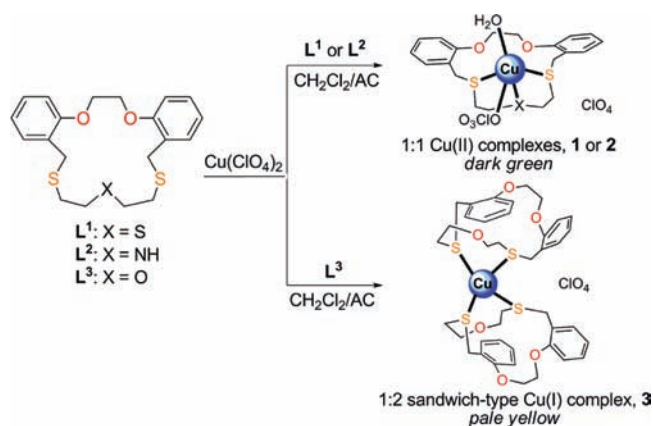
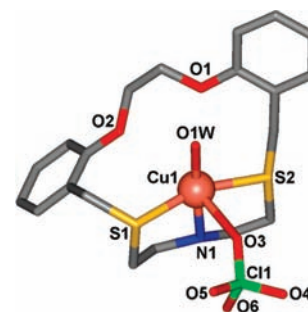
Cu1–O1W	1.956(3)	Cu1–S1	2.344(1)
Cu1–S2	2.271(1)	Cu1–S3	2.329(1)
Cu1–O3	2.757(1)	Cu1···O1	3.020(3)
Cu1···O2	2.806(3)		
O1W–Cu1–S1	95.8(1)	O1W–Cu1–S3	90.5(1)
S2–Cu1–S3	86.5(4)	S1–Cu1–S2	90.1(4)
O1W–Cu1–O3	85.7(1)	S1–Cu1–O3	72.1(1)
S2–Cu1–O3	99.5(1)	S3–Cu1–O3	76.3(1)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 2

Cu1–O1W	1.932(3)	Cu1–N1	2.006(6)
Cu1–S1	2.327(1)	Cu1–S2	2.351(1)
Cu1–O3	2.568(1)	Cu1···O1	3.332(3)
Cu1···O2	3.332(3)		
O1W–Cu1–S1	95.0(1)	O1W–Cu1–S2	93.9(1)
N1–Cu1–S1	85.4(2)	N1–Cu1–S2	84.3(2)
O1W–Cu1–O3	89.6(1)	S1–Cu1–O3	85.7(1)
S2–Cu1–O3	76.4(1)	N1–Cu1–O3	85.6(1)

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for 3

Cu1–S1	2.334(1)	Cu1–S2	2.306(1)
Cu1–S3	2.329(1)	Cu1–S4	2.322(1)
S1–Cu1–S2	104.4(5)	S1–Cu1–S3	108.6(5)
S1–Cu1–S4	115.5(4)	S2–Cu1–S3	114.3(5)
S2–Cu1–S4	109.8(5)	S3–Cu1–S4	104.5(5)

Scheme 1. Copper Complexes 1–3 Synthesized in the Present Study**Figure 1.** Crystal structure of the 1:1 [Cu(II)/ligand] complex 1, [Cu(L¹)(H₂O)(ClO₄)]ClO₄·acetone. The noncoordinating anion and solvent molecule are omitted.**Figure 2.** Crystal structure of the 1:1 [Cu(II)/ligand] complex 2, [Cu(L²)(H₂O)(ClO₄)]ClO₄. Hydrogen atoms and the noncoordinating anion are omitted.

results, in part, from the presence of weak interactions (2.806–3.332 Å) between each Cu(II) center and the two ether oxygen donors present in both L¹ and L².

Copper(I) Complex 3. In contrast to the behavior of L¹ and L², reaction of L³ with Cu(ClO₄)₂·6H₂O resulted in the initial green acetonitrile reaction mixture changing to colorless within a few minutes at room temperature. Slow evaporation of the colorless solution afforded a high yield of a bright yellow crystalline product, 3. The crystal color and elemental analysis of this product initially suggested that it was a Cu(I) species and this was subsequently

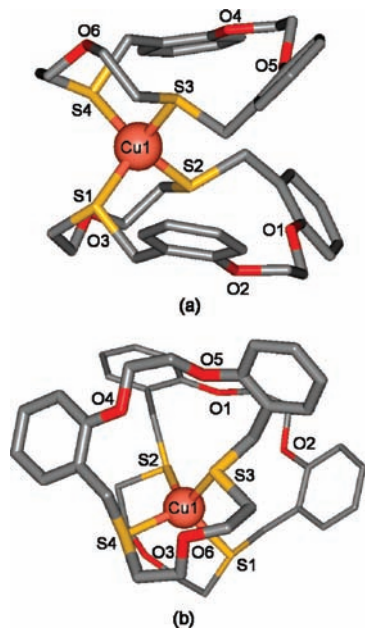


Figure 3. Crystal structure of the 1:2 [Cu(I)/ligand] sandwich-type complex **3**, [Cu(L³)₂](ClO₄)·acetone: (a) side view and (b) top view. Hydrogen atoms, noncoordinating anion, and solvent molecule are omitted.

confirmed by a crystal structure determination (see below).

Contrasting with the similar 1:1 stoichiometries of the Cu(II) complexes **1** and **2** derived from L¹ and L², the structure of the Cu(I) complex **3** confirms it to be a 1:2 (M/L) species of formula [Cu(L³)₂](ClO₄)·acetone in which no anion or solvent molecule is present in the coordination sphere. This complex exhibits an unusual sandwich-like structure in which the Cu(I) center has a distorted tetrahedral environment. Each macrocycle coordinates in a bidentate fashion via two exodentate S donors (Figure 3), with the X = O donor (and the remaining two ether oxygens of each ligand) remaining unbound. A search of the Cambridge Structural Database revealed other examples of similar noncoordination of O to Cu(I) when flanked by bound sulfurs in a –SCH₂CH₂–OCH₂CH₂S– sequence.^{5b,12} The S–Cu–S angles in the present structure vary from 104.43(4) to 115.45(4)°, while the Cu–S bonds fall in the range 2.306–2.334 Å—typical values for Cu(I)–S(thioether) bond lengths in tetrahedral complexes.¹³ In keeping with its symmetrical d¹⁰ electronic configuration and soft HSAB nature, Cu(I) has been previously well-documented to show a propensity for

forming strong complexes incorporating an S₄ tetrahedral coordination geometry,^{5b,14} and this presumably contributes to the thermodynamic driving force for the Cu(II) reduction observed on complexation in the present case.

In the present study, a simple change of the X donor atom from S in L¹ or NH in L² to O in L³ thus results in the complex of the latter ligand adopting both a new oxidation state and a different geometry relative to the corresponding complexes of L¹ and L². The low affinity of the electronegative X = O donor for the soft Cu(I) ion clearly aids the attainment of the tetrahedral geometry in the latter case. Thus, the noncoordination of the O in the –S–O–S– string of each bound L³ allows the formation of two large (eight-membered) chelate rings involving the central Cu and the two S donors of each ligand such that the necessary increased “bite” angle for tetrahedral coordination is readily accommodated. As a consequence, the Cu(I) center in this complex is readily stabilized by forming a 1:2 (M/L) complex that uses the two S donors from each L³ to adopt a favored (higher symmetry) tetrahedral S₄-donor set. In contrast, for L¹ (where X = NH) or L² (where X = S), all three donors of the –S–X–S– string readily coordinate to Cu(II) such that the observed 1:1, five-coordinate, cationic complexes of type [Cu(L¹)(H₂O)(ClO₄)]⁺, incorporating two adjacent five-membered chelate rings, are preferentially formed.

Mass Spectra of Complexes 1, 2, and 3. The 1:1 complex stoichiometry for L¹ and L² and the 1:2 stoichiometry for L³ observed in the above studies were also confirmed for these complexes by their fast-atom bombardment (FAB) mass spectra, which gave peaks corresponding to [Cu(L¹)(ClO₄)]⁺ (*m/z* 553.97), [Cu(L²)(ClO₄)]⁺ (*m/z* 537.01), and [Cu(L³)₂]⁺ (*m/z* 815.16), respectively (Figure 4). Inspection of the relative abundance isotope patterns for the latter peaks also showed the expected good agreement with their corresponding simulated peaks.

Cyclic Voltammetry. Preliminary cyclic voltammetric data for **1–3** yielded *E*_{pc} values for **1** and **3** of 0.57 and 0.52 V (Figure 5), while the scan for **2** was not reproducible under similar conditions, perhaps reflecting the presence of interfering adsorption phenomena.

Preliminary cyclic voltammetric data indicate that the *E*_{pc} value for **3** (Figure 5c) differs slightly from that for **1** (Figure 5b), probably reflecting the different geometrical structures present. The observed cathodic shift in the reduction potential of **3** on going from acetonitrile (*E*_{pc} = 0.52 V, Figure 5c) to dichloromethane (*E*_{pc} = 0.49 V, Figure 5d) is attributed to the extra stabilizing effect of the complex as a result of the lower donor capacity of dichloromethane compared to that of acetonitrile. Both the observed positive potentials (vs saturated calomel electrode) and the quasi-reversible/irreversible nature of the couples agree with the results for other sulfur-containing ligand systems that engender stabilization of copper in its +1 state.^{6b,15,16} For both complexes **1** and **3**, the current was directly proportional

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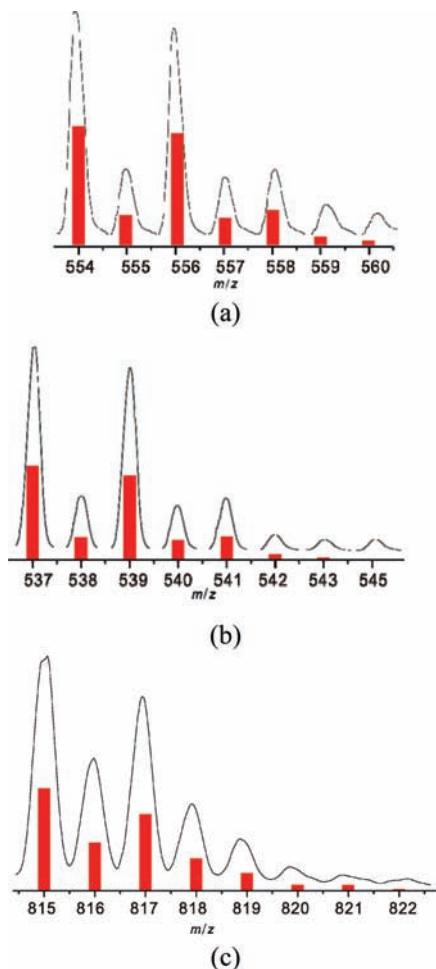


Figure 4. Observed isotope distributions in the FAB mass spectra for (a) $[\text{Cu}(\text{L}^1)(\text{ClO}_4)]^+$ in **1**, (b) $[\text{Cu}(\text{L}^2)(\text{ClO}_4)]^+$ in **2**, and (c) $[\text{Cu}(\text{L}^3)_2]^+$ in **3**. The bars represent the predicted mass spectral distribution for each ion.

to the potential scan rate over the range of 10–150 mV/s (see Figure S1, Supporting Information); **3** is more reversible than **1**, suggesting the existence of facile charge-transfer kinetics in this case.¹⁷

Solution Studies. Spectrophotometric titrations were carried out in acetonitrile (Figure 6) in order to probe the coordination (and potential redox) behavior of the above complexes in solution. As shown in Figure 6a,b, the titrations of L^1 and L^2 with $\text{Cu}(\text{ClO}_4)_2$ resulted in a gradual increase in intensity of the respective ligand-to-metal charge transfer bands at 417 and 413 nm as well as the d–d bands at 626 and 604 nm. The absorption spectra of **3** (Figure 6c) showed no evidence for the presence of d–d bands in the visible region but showed the rise of a π -ligand/metal-to-ligand charge transfer band at 312 nm in keeping with the sole formation of a Cu(I) species. Interestingly, repeating this experiment with L^1 and L^2 and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ substituted for $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ resulted in similar spectrophotometric behavior in each case to that observed with L^3 , confirming that both L^1 and L^2 are also capable of complexing Cu(I) under the conditions employed (see Figure S2, Supporting Information). This is perhaps not unexpected given that

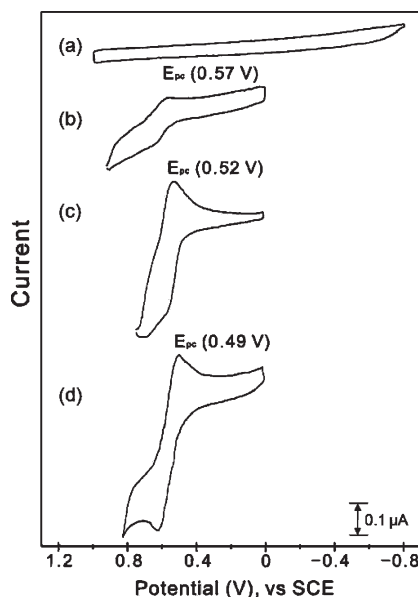


Figure 5. Cyclic voltammograms of 1.0 mM of (a) blank, (b) **1** in CH_3CN , (c) **3** in CH_3CN , and (d) **3** in CH_2Cl_2 . Measurement conditions: supporting electrolyte, 0.1 M Bu_4NClO_4 ; working electrode, platinum electrode; reference electrode, sodium saturated calomel electrode; and scan rate, 10 mV s^{-1} .

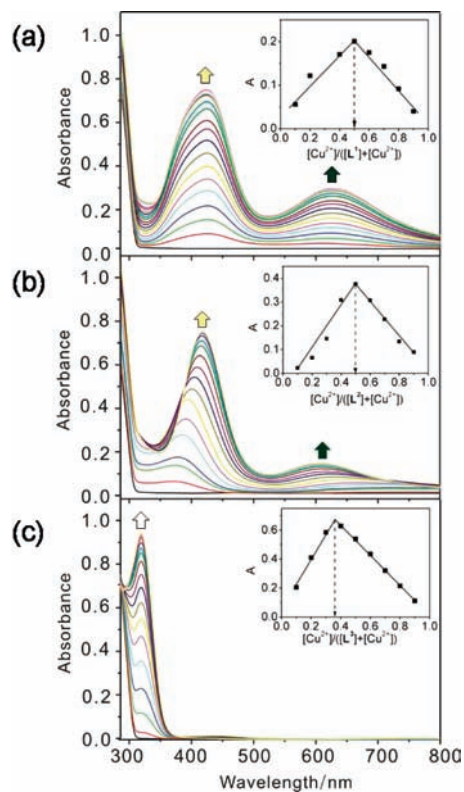


Figure 6. UV–vis titrations of (a) L^1 , (b) L^2 , and (c) L^3 with $\text{Cu}(\text{ClO}_4)_2$ in acetonitrile. Corresponding Job plots are shown in the insets; all measurements were taken after solution equilibrium had been established.

other Cu(I) complexes of S_2N - and S_3 -donor ligands have been documented previously.^{18,19}

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Paralleling the solid-state results, Job plots (based on the d–d region) for the complexation of Cu(II) with L^1 and L^2 in acetonitrile clearly indicate the formation of 1:1 (M/L) Cu(II) complexes, while the corresponding plot for L^3 (based on the UV absorption at 312 nm) is in accord with the formation of a Cu(I) species with a M/L ratio of 1:2—again corresponding to the stoichiometry observed in the corresponding X-ray structure.

In view of the observation that the reaction of L^3 with $Cu(ClO_4)_2$ in acetonitrile resulted in the spontaneous generation of a corresponding colorless Cu(I) complex, it was decided that a probe of the effect of a change of solvent on the observed color change was needed. Accordingly, the experiment using acetonitrile was repeated first substituting methanol and then ethanol for acetonitrile; in each case, the green reaction mixture was again observed to change to colorless (see Figure S3, Supporting Information). The rate of color disappearance was observed to be significantly faster for both these alcohols than found for acetonitrile. Unfortunately, solubility limitations prevented us from extending these studies to other common solvents.

In prior studies, the spontaneous reduction of Cu(II) on complexation to sulfur ligands was postulated to occur via the copper-catalyzed oxidation of the reaction solvent^{6b} (with in some cases the process being photo-assisted)²⁰ or via ligand oxidation involving generation of a thioether radical cation on the coordinated sulfur ligand employed.^{6c,21} In one study, both solvent oxidation and ligand oxidation (leading to sulfoxide formation) were demonstrated to occur (with the ligand oxidation postulated to proceed via the sulfur radical cation route—this pathway was demonstrated to dominate at lower temperatures).¹⁶ In this context, it is noted that Malachowski et al.^{6b} reported a study that yielded results in good agreement with ours—in their case, the spontaneous conversion of Cu(II) to Cu(I) was observed in the presence of a sterically demanding open-chain N_2S_2 ligand with, as found in the present study, the reduction rate being much greater in methanol than in acetonitrile. These workers assigned the observed redox behavior to involve solvent oxidation. While the exact electron source for the Cu(II)/Cu(I) reductions observed in the present study has not been defined with certainty, in keeping with the prior studies just mentioned, it seems extremely likely that solvent, possibly coupled with ligand oxidation, is again involved.

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In further studies, aimed at investigating the generality of the present observed redox behavior, additional spectrophotometric titration experiments were carried out in acetonitrile under identical conditions to those described earlier except that the 16- and 18-membered O_3S_2 -macrocyclic analogs, L^4 and L^5 , were substituted for (17-membered) L^3 . Each of these ligands was observed to promote a loss of the initial green color when mixed with $Cu(ClO_4)_2$ in acetonitrile at room temperature in a similar fashion to that observed for L^3 . The titrations involved the incremental addition of $Cu(ClO_4)_2$ to each L^4 and L^5 in acetonitrile while following the rise of an intense ligand transition in the UV region (at 303 and 315 nm, respectively; see Figure S4, Supporting Information). Again, evidence for the formation of a 1:2 (M/L) species (corresponding to a weak inflection in the respective titration curves) was observed in each case followed by the formation of a 1:1 species (in the presence of excess copper).

Conclusion

We have demonstrated that the change of a single donor atom from S or NH to O in the present macrocyclic systems results in a switch of the coordination geometry and oxidation state of the central copper ion in the corresponding complexes in both the solid state and in solution; in the process, we have generated an unusual sandwich-type Cu(I) complex of type $[Cu(L^3)_2]ClO_4$ of considerable intrinsic interest. In a limited number of prior studies, the spontaneous formation of Cu(I) species from corresponding Cu(II) precursors incorporating thioether-containing ligands involving oxidation either of the solvent or of the ligand has been reported. Our results make available three additional examples of this type. More generally, the results serve as a further illustration of the role that donor atom tuning may play in the control of oxidation state selectivity within the biologically important²² Cu(I)/Cu(II) redox system.

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Supporting Information Available: UV–vis titration data for copper complexation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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