1030 (1967); (e) E. E. van Tamelen and S. P. Pappas, *ibid.*, **85**, 3297 (1963); E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *ibid.*, **93**, 6092 (1971); E. E. van Tamelen and D. Carty, *ibid.*, **93**, 6102 (1971).
(9) The secondary conversion of **6** to benzene causes a variation in the observed ratio of benzene to **6** after extended photolysis. However, it appears that most of the benzene in the direct photolysis of **1** derives from S_1.
(10) Compound **1** quenches acetophenone phosphorescence at the diffusional rate in acetonitrile ($k_q = 8 \times 10^9\ M^{-1}\ s^{-1}$). At less than 10% conversion, $\phi = 0.3$ for the photosensitized decomposition of **1**. Benzene is also formed (33%), but, as in the direct photolysis,[9] may arise from photosensitized decomposition of **6**.
(11) The possibility of oxygen assisted $S_1 \rightarrow T_1$ conversion has been suggested previously, but not established definitely: W. D. Clark and C. Steel, *J. Am. Chem. Soc.*, **93**, 6347 (1971); G. L. Loper and F. Dorer, *ibid.*, **95**, 20 (1973).
(12) That this might be the case has precedent in the literature: P. D. Bartlett and N. A. Porter, *J. Am. Chem. Soc.*, **90**, 5317 (1968).
(13) The intermediacy of **3** in the thermolysis of **1** was previously considered as a possibility, but rejected because of the absence of **3** as product when **1** is pyrolyzed in the vapor phase.[6]
(14) Dewar benzene and its simple derivatives are generally chemiluminescent: P. Lechtken, R. C. D. Breslow, A. H. Schmidt, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 3025 (1973).
(15) A quantitative comparison of the chemiluminescence yield from **1** and **3** indicates that if **3** is formed it must be produced in high yield in order to account for the observed chemiluminescence intensity. That **3** is formed is corroborated by the observation that the ratio of indirect chemiluminescence from DBA and 9,10-diphenylanthracene is identical when **3** or **1** is the source of chemiexcitation. That benzene triplet is the chemiexcited species involved is corroborated by the observation that the Stern–Volmer constant for the quenching of chemiluminescence by *cis*-butene is the same as for the quenching of benzene triplet by *cis*-butene.
(16) The competition between fluorescence and intersystem crossing in cyclic azo compounds varies widely with structure, Dr. K.-C. Liu, Columbia University, unpublished results. Indeed, some [2.2.2]diazabicyclooctenes possess fluorescence yields approaching unity. Clearly, nitrogen cleavage will be efficient only at temperatures at which the activation barrier to C–N cleavage in S_1 is overcome.
(17) An intriguing possibility is that the contrasting behavior of S_1 and T_1 may be due to an *adiabatic* photoreaction of T_1 to some triplet of **6** or its precursor. This possibility is presently under investigation.

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Redox Properties of Copper–Thiaether Complexes. Comparison to Blue Copper Protein Behavior

Sir:

The unique spectral and redox properties of blue copper proteins have been the subject of much interest, particularly since, until recently, they eluded duplication by model complexes.[1,2] In a recent communication[3] we reported the first examples of low molecular weight Cu(II) complexes, involving a series of cyclic and open-chain polythiaethers, which exhibit an intense absorption band in the 600-nm region, the hallmark of the blue copper proteins. Ancillary crystallographic structural studies[4] and single crystal spectra[5] indicate that this characteristic absorption band results from a thiaether sulfur-to-copper charge transfer band *which is not dependent on coordinative distortion* as had been previously suggested.[6,7]

Markedly positive Cu(II)-Cu(I) formal electrode potentials (+0.2 to +0.8 V vs. SHE at pH ~7) have also been a recognized characteristic of the blue copper proteins, the source of which has long been in controversy.[8,9] Ligands which sterically or electronically destabilize tetragonal Cu(II) and/or enhance the stabilization of Cu(I) can shift the formal Cu(II)-Cu(I) reduction potential to more positive values.[10] Many workers have suggested that either tetrahedral or trigonal bipyramidal coordination is implied by the high redox potentials (and spectral properties) of the blue copper proteins.[6,7] In pursuing this hypothesis, Patterson and Holm recently examined a broad series of Cu(II) complexes to identify specific ligand structural features which might give rise to Cu(II)-Cu(I) potentials in the blue copper protein range.[11] However, most of the 37 complexes examined by them exhibited negative potentials with respect to SHE.

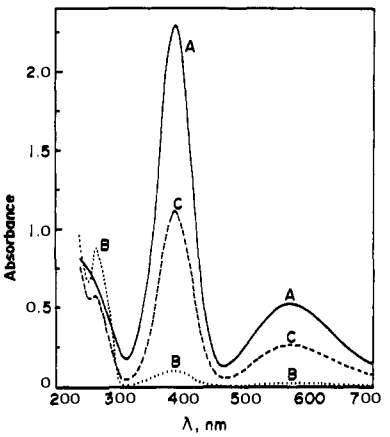


Figure 1. Absorbance spectra (1-cm cell) of a solution containing 5.68×10^{-4} M total copper ion and 5.59×10^{-4} M total 14-ane-S_4 ligand (L) in a matrix of 0.1 M $HClO_4$ in 80% methanol–20% water (by weight). Curve A represents the initial solution: $[Cu(II)L] = 2.69 \times 10^{-4}$ M, $[Cu(II)] = 2.99 \times 10^{-4}$ M, $[L] = 2.90 \times 10^{-4}$ M. Curve B represents the same solution after 85% reduction by electrolysis at 0.45 V (vs. SHE); $[Cu(I)L] = 4.75 \times 10^{-4}$ M, $[Cu(II)L] = 1.25 \times 10^{-5}$ M, $[Cu(II)] = 8.0 \times 10^{-5}$ M, $[L] = 7.1 \times 10^{-5}$ M. (Note the Cu(I) peak at 265 nm.) Curve C represents the reduced solution after exposure to air for 1 week showing partial reoxidation. Curve A is completely regenerated either by continued exposure to air or by oxidative electrolysis.

We wish to report at this time the results of a systematic investigation on the redox properties of a series of Cu(II)-polythiaether and polyaminothiaether complexes which exhibit redox potentials in the blue copper protein range *independent of coordinative geometric constraints.* The ligands studied include the seven cyclic and one open-chain species for which the spectral properties of the Cu(II) complexes were previously reported[3] plus eight closely related species (Table I). All ligands were synthesized and purified by established procedures[12] or modifications thereof. Due to the sparing solubility of the 12 polythiaether compounds in water, all redox measurements were carried out in 80% CH_3OH–20%H_2O (by weight), corresponding to the conditions utilized for our previous spectral[3] and kinetic[13] studies on these systems.

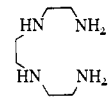
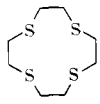
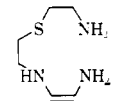
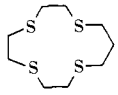
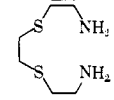
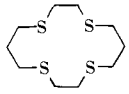
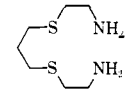
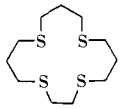
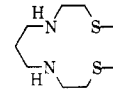
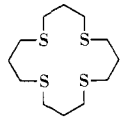
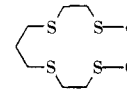
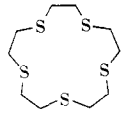
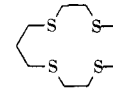
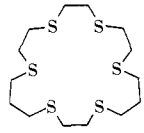
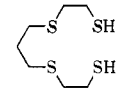
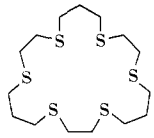
For each of the Cu(II) complexes studied, $E_{1/2}$ values were estimated from cyclic voltammetric measurements (platinum electrode system) in which cathodic and anodic peaks were identified for the process:

$$Cu^{II}L + e^- = Cu^{I}L$$

where L represents the coordinated polythiaether or polyaminothiaether ligand. To confirm the nature of the redox process involved, Cu^{II}(14-ane-S_4) was completely reduced by controlled potential coulometry at +0.45 V (vs. SHE) requiring 1.00 ± 0.02 electrons per equivalent of complex. The reduced solution yielded cyclic voltammetric behavior which was virtually identical with that of the original solution ($E_{1/2} = 679 \pm 10$ mV). This Cu(I) solution exhibited no visible spectrum but showed an absorption peak in the ultraviolet region (Figure 1, curve B). That this peak is characteristic of Cu(I) was confirmed by measuring the spectrum of an aqueous solution (deaerated) of CuCl in 0.1 M $HClO_4$. Reoxidation of the Cu^{I}(14-ane-S_4) solution at +0.95 V (vs. SHE) regenerated the original spectrum (see Figure 1) indicating that the ligand structure was not disrupted by the electrolysis. The reduced complex was found to be stable over a period of several weeks under N_2 atmosphere but when exposed to air is slowly reoxidized to Cu^{II}(14-ane-S_4) (see Figure 1).

As shown in Table I, all of the $E_{1/2}$ values for the polythiaether complexes S_3 to S_6 are in the range of +0.67 to 0.90 V (vs. SHE) among the highest values reported for the

Table I. Redox Potentials for Copper(II) Complexes with Cyclic and Open-Chain Polythiaethers and Aminothiaethers in 80% Methanol–20% Water (by wt.) at 25 ± 1°. μ = 0.1 M ($HClO_4$)

Cyclic ligand complexes			Open-chain ligand complexes		
Coordinated ligand	Ligand abbrev[a]	$E_{1/2}$, mV[b]	Coordinated ligand	Ligand abbrev[a]	$E_{1/2}$, mV[b]
	12-ane-S_3	789 ± 10		2,2,2-N_4 (trien)	−280 ± 10
	12-ane-S_4	723 ± 10		2,2,2-NSNN	356 ± 22[c]
	13-ane-S_4	674 ± 10		2,2,2-NSSN (eee)	361 ± 19[c]
	14-ane-S_4[d]	689 ± 12		2,3,2-NSSN (ete)	312 ± 20[c]
	15-ane-S_4	785 ± 9		Et_2-2,3,2-SNNS	342 ± 20[c]
	16-ane-S_4	798 ± 15		$Et_2$2,3,2-S_4	892 ± 10
	15-ane-S_5	855 ± 10		Me_2-2,3,2-S_4	892 ± 10
	20-ane-S_6	805 ± 10		2,3,2-S_4 (TTU)	~842
	21-ane-S_6	852 ± 20			

[a] For ligand nomenclature, see ref 3 and 13. [b] $E_{1/2} = (E_p^a + E_p^c)/2$. [c] Potential values of mixed-donor ligand complexes show no significant dependence on acidity over the range pH* 2.7–7.7 (for explanation of nonaqueous pH* scales, see D. B. Rorabacher, W. J. MacKellar, F. R. Shu, and M. Bonavita. *Anal. Chem.* 43, 561 (1971). [d] Current parameters determined for 14-ane-S_4 at sweep rates of 7–360 mV s^{-1}: i_p^c/i_p^a = 1.00 ± 0.03, $i_p^c/v^{1/2}$ = (3.00 ± 0.29) × 10^{-5} A $s^{1/2}$ $V^{-1/2}$, $i_p^a/v^{1/2}$ = (2.96 ± 0.25) × 10^{-5} A $s^{1/2}$ $V^{-1/2}$.

Cu(II)-Cu(I) couple. Comparison of the data for the cyclic tetrathiaether ligands (i.e., *n*-ane-S_4 series) indicates a slight dependence on ligand ring size with a minimum in $E_{1/2}$ values for the complexes involving the 13- and 14-member rings. Since the latter Cu(II) complex has been shown to have regular tetragonal coordination[4] while the former complex appears to be distorted,[14] the large Cu(II)-Cu(I) potentials *do not appear to be primarily dependent on coordinative distortion.*

Comparison of the cyclic S_3, S_4, S_5, and S_6 complexes shows some variations in potential with the number of available donor atoms. However, these are not dramatically larger than the ring size dependencies noted for the S_4 ligands and may be attributable to similar ring strain effects.

Of particular note are the potentials exhibited by the open-chain ligand complexes. The two open-chain tetrathiaether complexes exhibit the most positive potentials observed. However, a reduction in the number of available sulfur donors to two or one is accompanied by a dramatic (0.5 V) decrease in potential. Furthermore, the elimination of the last sulfur donor atom (e.g., as in $Cu(trien)^{2+}$) results in a further (~0.6 V) decrease to negative potential values.

Of added significance is the observation that the complex of 2,3,2-S_4 (TTU), involving both thiaether and mercaptide sulfur donor atoms, exhibits a potential similar to the corresponding open-chain tetrathiaether complexes and is vastly different from the complex of the corresponding diaminodithiaether, 2,3,2-NSSN (ete). This implies that *coordination to either mercaptide sulfur or thiaether sulfur may produce a similar influence on the Cu(II)-Cu(I) potential.*

Among the blue copper proteins, the blue electron carriers contain a single copper ion. Of these, the azurins and plastocyanins (all of which contain one or more methionine and one or more cysteine residues) are reported to exhibit potentials in the range of +0.23 to +0.37 V.[15] Based on our observations, the potentials of these proteins could be wholly accounted for by coordination to one thiaether sulfur donor atom (from a methionine residue) with no coordinative distortion required. Based on the limited data involving mercaptide sulfur, cited above, these potentials could also be attributable to a single coordinated cysteine residue. (Interestingly, however, stellacyanin, with no available methio-

nine residues,[16] exhibits a potential of only +0.18 V[15] which does not differ significantly from the aquocopper value.[17])

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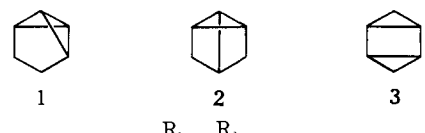
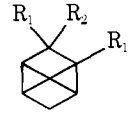
The Photochemical Synthesis of a Tricyclo[2.2.0.0^{2,5}]hexane[1]

Sir:

A considerable amount of research on small ring compounds has been devoted to the study of tricyclohexane ring systems. A number of papers have been published in recent years on the synthesis and properties of compounds possessing the highly strained tricyclo[3.1.0.0^{2,6}]-, tricyclo[2.2.0.0^{2,6}], and tricyclo[3.1.0.0^{2,4}]hexane structures **1, 2,** and **3**.[3-18] In this communication we wish to report the first successful synthesis of a compound, which possesses the hitherto unknown tricyclo[2.2.0.0^{2,5}]hexane ring (**4a**), namely, 1,2-diphenyltricyclo[2.2.0.0^{2,5}]hexan-2-ol (**4b**). Our synthesis consists of five steps from 2-phenylbicyclo[1.1.1]pentan-2-ol (**5**),[19] and affords the tricyclohexanol (**4b**) in 20% overall yield.



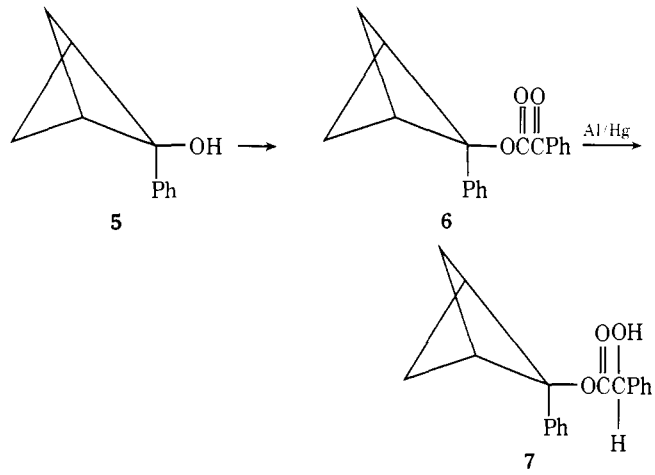
1 2 3



4a, $R_1 = R_2 = H$
4b, $R_1 = Ph$; $R_2 = OH$

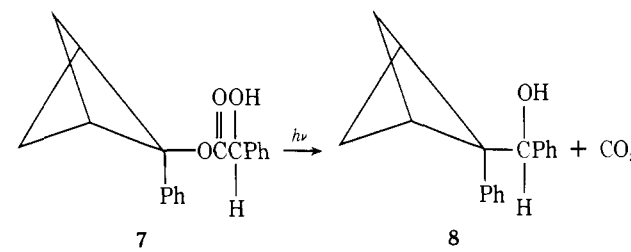
2-Phenylbicyclo[1.1.1]pentane 2-benzoylformate (**6**) was prepared by stirring an equimolar mixture of 2-phenylbicyclo[1.1.1]pentan-2-ol (**5**), benzoyl formic acid chloride,[20] and pyridine at 10 °C for 1 h in benzene. The benzoylformate ester **6** was recrystallized from petroleum ether and was isolated as a white crystalline solid mp 63-64 °C (ir (CCl_4) 3.34, 3.45, 5.77, 5.91, 6.25 μ; NMR (CCl_4) methylene δ 2.61 (doublet of doublets J = 2.7, 10.3 Hz (1 H)), 1.58 (doublet of doublets J = 3.0, 10.3 Hz (1 H)), 1.89 (doublet J = 2.7 Hz (1 H)), 1.72 (doublet J = 3.0 Hz (1 H)), bridgehead δ 3.37 (singlet (2H)), aromatic δ 7.30 (multiplet (8 H)), 7.86 (multiplet (2 H)).

Upon treatment with aluminum amalgam in wet ether, ester **6** was reduced quantitatively to the mandelate ester **7.** Ester **7** is a white solid mp 127-128° (ir (CCl_4) 2.82, 3.32, 5.78 μ; NMR (CCl_4) methylene δ 1.94 (doublet of doublets J = 3.0, 10.5 Hz (1 H)), 1.48 (doublet of doublets J = 2.5, 10.5 Hz (1 H)), 1.61 (overlapping doublets (2 H)), bridgehead δ 3.25 (singlet (2 H)), benzyl δ 4.87 (singlet (1 H)), aromatic δ 7.20 (multiplet (10 H))).



5 6 7

Irradiation of a 0.004 M solution of **7** in *tert*-butyl alcohol at 2537 Å for 5 h led to decarboxylation[21] and afforded the bicyclopentylphenylcarbinol **8** (20%). The carbinol **8** was purified by silica gel chromatography and was isolated as a colorless oil (ir (CCl_4) 2.80, 3.40, 6.28 μ; NMR (CCl_4) methylene δ 3.27 (doublet of doublets J = 3.5, 10.5 Hz (1 H)), 1.87 (doublet of doublets J = 2.2, 10.5 Hz (1 H)), 2.17 (doublet J = 3.5 Hz (1 H)), 1.31 (doublet J = 2.2 Hz (1 H)), bridgehead δ 3.05 (doublet J = 18.0 Hz (1 H)), 3.38 (doublet J = 18.0 Hz (1 H)), benzyl δ 5.57 (singlet (1 H)), aromatic δ 6.90 (multiplet (9 H)), 6.07 (doublet J = 7 Hz (1 H)); *m/e* 232, 143 (base peak), 128, 107, 79, 77.



7 8

Oxidation of the carbinol **8** in acetone with 0.7 M Jones reagent[23] afforded 2-phenyl-2-benzoylbicyclo[1.1.1]pentane