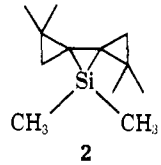
34% yield. An increase in the diene concentration resulted in a decrease in the yield of the silacyclopentene, and none of this product was obtained when the hexamethylsilirane–2,3-dimethyl-1,3-butadiene reaction was carried out (15 hr at 70°) in the absence of a diluent, although the tetramethylethylene yield was 40%. With some other dienes (e.g., *trans,trans*-2,4-hexadiene) no dimethylsilylene adducts were obtained under the conditions found to be successful with 2,3-dimethyl-1,3-butadiene. One may speculate that the unconverted 1,3 diene present in these reactions intercepts either a diradical intermediate[12a,b] of the rearrangement of the vinylsilacyclopropane or reacts (by cycloaddition?) with the product of the rearrangement. Further experiments are required on this point.

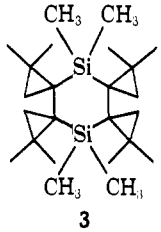
This new, mild route to dimethylsilylene may allow the development of new silylene chemistry, and experiments directed toward this goal are in progress. However, it should be recognized that the scope of the application of hexamethylsilirane will be limited by the extremely high reactivity of the silacyclopropane ring system toward many classes of compounds,[6,14-16] among which are some which might react with silylenes. In those cases reactions with the silirane starting material would preclude observation of the desired silylene reactions.

This thermal dimethylsilylene extrusion from hexamethylsilirane finds parallels in some known cases of sulfur extrusion from thiiranes[17] and in thermal difluorocarbene extrusion from *gem*-difluorocyclopropanes.[18] The other known silacyclopropanes[14] are much more thermally stable than hexamethylsilirane and do not serve as sources of dimethylsilylene at these low temperatures. Thus when **2**



2

was heated in triethylsilane solution at reflux for 17 hr, no $Et_3SiSiMe_2H$ was obtained, Instead, a 20% yield of a dimer of **2,** presumably **3,** was formed, along with nonvolatile polymeric material.



3

No information concerning the mechanism of dimethylsilylene extrusion from hexamethylsilirane is available at present. A concerted process, the reverse of singlet state silylene addition to the C=C bond,[12] seems a good possibility, but a stepwise process proceeding via the diradical $\cdot SiMe_2CMe_2CMe_2\cdot$ also must be considered.

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Macrocyclic Ligand Ring Size Effects on Complex Stabilities and Kinetics. Copper(II) Complexes of Cyclic Polythiaethers

Sir:

Much recent interest has centered on the unusually large stabilities of macrocyclic ligand complexes, particularly those of the cyclic polyethers (crown ethers) and cyclic tetramines, as compared to the corresponding open-chain species, and the dependency of these stabilities on ligand ring size.[1-4] Busch and co-workers[2] have attributed these enhanced stabilities to factors which they have called *multiple juxtapositional fixedness* (essentially configurational effects) in which emphasis has been placed on the relative rigidity of the complexed cyclic ligands resulting in an apparent increase in the difficulty of sequentially breaking the metal–donor atom bonds. Hinz and Margerum,[5] in dealing with a series of tetramines, have suggested that an additional and more dominant contribution arises in hydrogen-bonding ligands from the fact that the free cyclic species are less extensively solvated than their open-chain analogues and, thus, are thermodynamically more favored to exist in the complexed state since less solvation energy (primarily an enthalpic contribution) is involved. However, their study was unable to differentiate specifically between the contributions of solvation effects and configurational effects in the complexes studied, particularly since each of these effects likely contain both enthalpic and entropic contributions.

To date the supporting evidence for these effects has been limited to thermodynamic and indirect kinetic data. Direct kinetic data have been difficult to obtain since the cyclic polyethers form extremely labile complexes[6] while the polyamines protonate in the pH regions accessible to the solvated metal ions of general interest thereby introducing interfering electrostatic and conformational effects which are difficult to isolate.[7] A recent attempt to eliminate polyamine protonation by operating in 0.2–2.0 *M* NaOH media

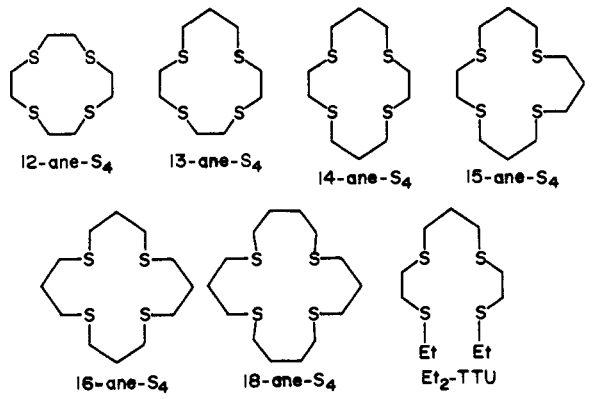

Figure 1. Tetrathiaethers included in this study.

Table I. Kinetic and Equilibrium Data for Copper(II) Reacting with Macrocyclic Tetrathiaethers in 80% Methanol at 25°, $\mu = 0.10\ M$ ($HClO_4$)

Ligand	Kinetic method[a]	k_f (M^{-1} sec^{-1})	k_d (sec^{-1})	K_{ML} (kinetic)	K_{ML} (equil)
12-ane-S_4	SF	1.2×10^3	4.4	2.7×10^2	3.3×10^2
13-ane-S_4	SF	1.4×10^4	51.	2.7×10^2	---
14-ane-S_4	SF, TJ	2.8×10^4	9	3.1×10^3	3.0×10^3
15-ane-S_4	TJ	4.3×10^4	1.9×10^2	2.3×10^2	---
16-ane-S_4	TJ	2.9×10^4	3.2×10^3	9	11
18-ane-S_4		---[b]	---[b]	---	$\ll 10$
Et_2-TTU	TJ	4.1×10^5	3.0×10^4	14	13

[a] Key: SF = stopped-flow; TJ = temperature-jump. [b] Complex too weak to allow kinetic study.

did, in fact, yield the intriguing observation that corresponding open-chain and cyclic polyamines exhibit nearly identical formation rate constants with $Cu(OH)_3^-$ as the reacting electrophilic species while with $Cu(OH)_4^{2-}$ the open-chain compound reacted about tenfold faster.[8] However, stability and dissociation rate constants were not obtained in that study making it impossible to examine the overall impact of ligand cyclization upon the complexation process.

We wish to report at this time the results of a complete kinetic and stability study of solvated copper(II) ion reacting with a third series of macrocyclic ligands incorporating homologous donor atoms, the cyclic polythiaethers. These ligands are free of protonation considerations and the copper(II) complexes are sufficiently weak to permit both the formation and dissociation rate constants to be obtained from direct measurements. Moreover, in contrast to the polyamines, neither the cyclic nor open-chain polythiaethers should be significantly solvated making it possible to examine directly the configurational contributions to the macrocyclic effect.

The specific ligands studied include the 12-, 13-, 14-, 15-, 16-, and 18-membered macrocyclic tetrathiaethers, viz., 1,4,7,10-tetrathiacyclododecane (12-ane-S_4); 1,4,7,10-tetrathiacyclotridecane (13-ane-S_4); 1,4,8,11-tetrathiacyclotetradecane (14-ane-S_4); 1,4,8,12-tetrathiacyclopentadecane (15-ane-S_4); 1,5,9,13-tetrathiacyclohexadecane (16-ane-S_4); and 1,5,10,14-tetrathiacyclooctadecane (18-ane-S_4); along with the closely related open-chain ligand 3,6,10,13-tetrathiapentadecane (Et_2-TTU).[9] The seven compounds studied are illustrated in Figure 1.

Due to the sparing solubility of all seven compounds in water, the kinetic and equilibrium studies were conducted in 80% CH_3OH–20% H_2O (by wt). In this medium the reactions were found to be independent of acidity (at constant perchlorate ion concentration) from 0.10 M $HClO_4$ to pH* 6[10] supporting the contention that the reactive species are solvated Cu(II) and the unprotonated ligands.

Table I lists the experimental data for the reaction process:

$$Cu^{2+} + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} CuL^{2+}$$

In agreement with previous studies on the tetramines,[2] the 14-membered macrocycle exhibits the largest stability constant while increasing ring size yields steadily diminishing stabilities. However, the kinetic data reveal that the formation rate constants of the 13- through 16-membered macrocyclic complexes are relatively constant. Thus the stability constants are primarily affected by the varying k_d values which exhibit a striking increase for the larger macrocycles and the open-chain species.

That these trends are not peculiar to this solvent composition has been established in ongoing studies in which the solvent composition is being varied systematically from 25 to 95% CH_3OH. Moreover, other work in progress in this laboratory reveals that the solvent trends in the *formation* rate constant are essentially independent of the ligand, being a characteristic of the Cu(II) solvation. Thus the trends observed in Table I are not attributable to solvent dependent conformational equilibria.

An independent study in progress in this laboratory has established that, under equivalent experimental conditions, the formation rate constant for Cu(II) reacting with NH_3 is about $2 \times 10^7\ M^{-1}$ sec^{-1}.[11] The 50-fold reduction in the k_f value for Cu(II) reacting with Et_2-TTU exactly reflects the anticipated steric hindrance associated with secondary donor atoms compared to unsubstituted donors[12] suggesting that first-bond formation is rate-determining with Et_2-TTU.

Recent crystallographic evidence shows that uncomplexed cyclic tetrathiaethers readily assume the exo conformation[13] (i.e., sulfur electron pairs pointing away from the ring center) such that steric hindrance arising from conformational effects[7] should be minimal with respect to first-bond formation. Thus the additional reduction in k_f values for the cyclic ligands strongly suggests that the rate-determining step is shifted to the point of second-bond formation as a result of the added steric constraint affecting this step.[12] With the possible exception of the 12-ane-S_4 ligand, this conclusion is strongly supported by the direct correlation of the ratios in k_f values for Et_2-TTU and the cyclic compounds to that previously observed in the study of $Cu(OH)_4^{2-}$ reacting with the corresponding tetramines wherein similar conclusions were reached.[8] Therefore, the *dependence of the dissociation rate constants and stability constants upon the size of the ring appears to be associated with the bonding of the third and fourth donor atoms and associated conformational changes* (e.g., folded to planar conformational inversions). As the ring size increases, the constraints of the ring diminish, thereby diminishing the macrocyclic effect.

The general conclusions which result from the foregoing considerations may be summarized as follows.

(i) The contribution of configurational effects (which are presumed to be primarily entropic) to the thermodynamic macrocyclic effect is manifested in the dissociation rate constant and is particularly associated with the initial stages of the dissociation process.

(ii) Since configurational effects must be primarily a function of the ligand backbone, this contribution to the macrocyclic effect should exist for all classes of macrocyclic ligands including polythiaethers, polyamines, polyethers (i.e., crown ethers), and mixed donor species. However, the magnitude of the configurational effects may vary from class to class as a result of conformational differences in the complexed ligands resulting from variations in the coordi-

nate bond lengths exhibited with various types of donor atoms (e.g., Cu-N bonds = 1.95 Å in $Cu(14\text{-ane-}N_4)(ClO_4)_2$, while Cu-S bonds = 2.30 Å in $Cu(14\text{-ane-}S_4)(ClO_4)_2$).[14]

(iii) The similarity in k_f ratios exhibited by the corresponding open-chain and cyclic ligands for both the polyamines and polythiaethers implies that any ligand solvation effects contributing to the macrocyclic effect in the polyamine complexes must be manifested kinetically in the dissociation rate constants. Thus it is inferred that it is the difference in the solvation of complexed and partially bonded open-chain and cyclic ligands which gives rise to the reported solvation effects while the solvation of the uncomplexed and partially bonded species are not significantly different for the two ligand types.

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Evidence for Metastable Five-Coordinate Cobalt(III) Intermediates

Sir:

The induced aquation of *trans*-MN_3Cl^+ (where M designates the $Co^{III}(en)_2$ group) with NO^+ gave (27 ± 3)% *cis*-MH_2OCl^{2+} and the rest trans product[1] and the induced aquation of *trans*-MCl_2^+ with Hg^{2+} gave (28 ± 5)% *cis*-MH_2OCl^{2+} and the rest trans product.[2] The induced aquation of *cis*-MN_3Cl^+ with NO^+ gave (79 ± 2)% *cis*-MH_2OCl^{2+} and the rest trans product[3] and the induced aquation of D-*cis*-MCl_2^+ with Hg^{2+} gave approximately 70% D-*cis*-MH_2OCl^{2+} and the rest trans product.[2] It is obvious that the induced aquations of the cis and trans reactants do not pass through a common nuclear configuration before the aquo-products are formed from the reactants. A trigonal bipyramidal intermediate with equatorial Cl^- directing ligand has been postulated for the induced aquations of the cis reactants[2,3] and a square pyramidal intermediate for those of the trans reactants. Here the two different intermediates will be designated as *c*-MCl^{2+} and *t*-MCl^{2+} only for the purpose of indicating that they came from cis reactants and from trans reactants, respectively. Several different explanations are advanced below for the lack of a common nuclear configuration for the *c*-MCl^{2+} and *t*-MCl^{2+} moieties which depend on the lifetimes of these five-coordinate cobalt(III) moieties. Strong evidence will be reported here for the existence of the metastable intermediates described in the fourth explanation.

First, the five-coordinate MCl^{2+} moieties may exist only in activated complexes with the sixth ligand (H_2O) being attached as the point representative of the reacting system moves "downhill" from the activated complex region to the product region of phase space.

Second, the *c*-MCl^{2+} and *t*-MCl^{2+} intermediates may exist only long enough to survive a few collisions in escaping the solvent cages in which they were formed and, during this short lifetime, are changing toward a common intermediate but do not reach it before attaching the sixth ligand to form products.

Third, the two intermediates may have a lifetime shorter than the solvent cage lifetime ($<10^{-10}$ sec), so they cannot "hunt" for different nucleophiles in the bulk solution, nor do they relax toward a common configuration during this lifetime.

Fourth, the two intermediates may have sufficient stability to survive many collisions in diffusing through the solution and hence to rather selectively react with a choice of nucleophiles. We present evidence for this last explanation from an investigation of the competition reactions of the five-coordinate cobalt(III) moieties for H_2O and Cl^- in aqueous chloride solutions. The facts are these.

(1) The ratio of *trans*-MCl_2^+/*cis*-MCl_2^+ products formed from the *trans*-$MN_3Cl^+ + NO^+$ reaction does not decrease with decreasing Cl^- concentration in the range 2.0 $M \geq [Cl^-] \geq 0.5$ M and no measurable amounts of the cis isomer are formed; all entering Cl^- ligands go in trans to the directing Cl^- group.

(2) The ratio of *trans*-MH_2OCl^{2+}/*cis*-MH_2OCl^{2+} formed from the *trans*-$MN_3OH_2^{2+} + NO^+$ reaction is approximately equal to 4 and does not decrease with decreasing Cl^- concentration in the 0.5–2.0 M range.

(3) The ratio of *trans*-MH_2OCl^{2+}/*cis*-MH_2OCl^{2+} formed from the *cis*-$MN_3OH_2^{2+} + NO^+$ reaction does not increase with decreasing Cl^- concentration in the same range and no measurable amounts of trans isomer are formed; all entering Cl^- ligands go in cis to the directing H_2O group.

(4) The ratio of *cis*-MH_2OCl^{2+}/*trans*-MH_2OCl^{2+} formed from the *cis*-M(DMSO($Cl^{2+} + MnO_4^-$ reaction (DMSO = dimethyl sulfoxide) is the same as from the *cis*-$MN_3Cl^+ + NO^+$ and *cis*-$MCl_2^+ + Hg^{2+}$ reactions.[2,3]

(5) The ratio of *trans*-MCl_2^+/*cis*-MCl_2^+ formed from the *cis*-M(DMSO)$Cl^{2+} + MnO_4^-$ reaction does not increase with decreasing Cl^- concentration and no measurable amounts of the trans isomer are formed; all entering Cl^- ligands go in cis to the directing Cl^- group.

Fact 1 indicates that *t*-MCl^{2+} does not fit the second explanation because *t*-MCl^{2+} has to live longer at low Cl^- concentrations than at high Cl^- concentrations in order to react with Cl^- yet the product ratio *trans*-MCl_2^+/*cis*-MCl_2^+ does not begin to approach that formed from *c*-MCl^{2+}.

Facts 2 and 3 also indicate that the *t*-MOH_2^{3+} and *c*-