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Zinc(II)-bound thiolate complexes-containing cysteine derivatives modeling of *methionine synthase* alkylating enzyme

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The reaction of thioimidazolylborate-zinc(II)-perchlorate complex [$Tt^{xyly} \cdot$ Zn-$OClO_3$] **1** (Tt^{xyly} = hydrotris[*N*-xylyl-thioimidazolyl]borate) with cysteine and its derivative *N*-acetyl cysteine and *S*-methyl cysteine leads to the formation of three new monomeric and dimeric thiolate complexes: [$Tt^{xyly} \cdot$ Zn-Cys-Zn $\cdot$ Tt^{xyly}] **2**, [$Tt^{xyly} \cdot$ Zn-Cys(NAc)-Zn $\cdot$ Tt^{xyly}] **3**, and [$Tt^{xyly} \cdot$ Zn-Cys(SMe)] **4**. The attachment of the cysteine derivatives to the Tt $\cdot$ Zn unit serves as structural models for the active site of *methionine synthase*. Methylation of the coordinated thiolate in the dinuclear zinc(II) complex **2** with methyl iodide appears to occur intramolecularly at the zinc-bound thiolates, forming methyl thioether-containing zinc(II) complex [$Tt^{xyly} \cdot$ Zn-Cys(SMe)] **4** and iodo complex [$Tt^{xyly} \cdot$ Zn-I] **5** with a clean second-order reaction of $k = 1.0 \times 10^{-5}\ M^{-1}\ s^{-1}$.

Keywords: biomimetic; zinc(II)-bound thiolate complexes; cysteine derivatives; *methionine synthase*; alkylation

1. Introduction

The coordination of zinc in a cysteine-ligated environment is a prominent feature of structural and functional sites of many important metalloproteins. Examples of such enzymes include the *Ada* repair protein (*1*, *2*), the *cobalamine*-dependent and -independent *methionine synthase* (*3*). One of the approaches, adapted to resolve the nature of the active site in these thiolate-alkylating zinc enzymes, has been to design various types of zinc complexes to account for or to mimic the functions of the central zinc (*4*).

Our previous publications to the modeling of biological thiolate alkylations (Scheme 1) (*5–16*) have outlined our approach and given ample reference to the valuable contributions of Vahrenkamp and coworkers (*11–19*), Darensbourg and coworkers (*20*), Parkin and coworkers (*4*, *21–24*), Carrano and coworkers (*25–31*), and Riordan and coworkers (*32*, *33*). They all verified and complemented the proposals and observations that the methylation occurs intramolecularly at the zinc-bound state in the thiolate model complexes.

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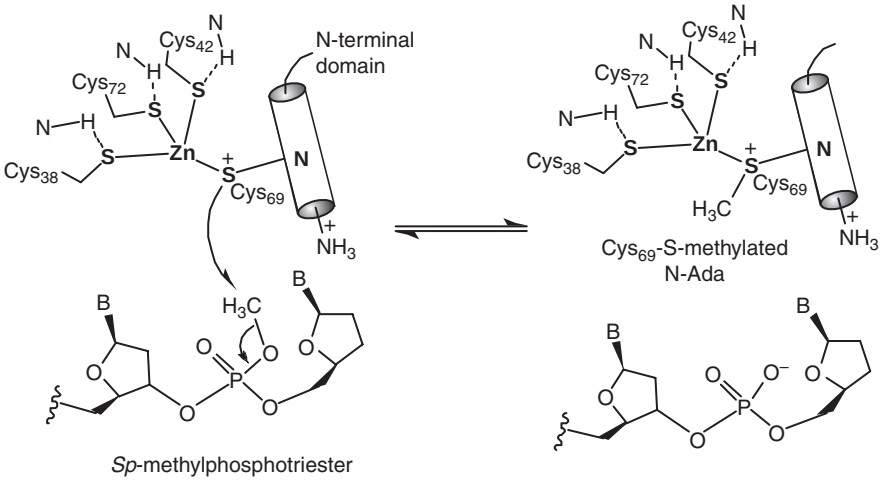
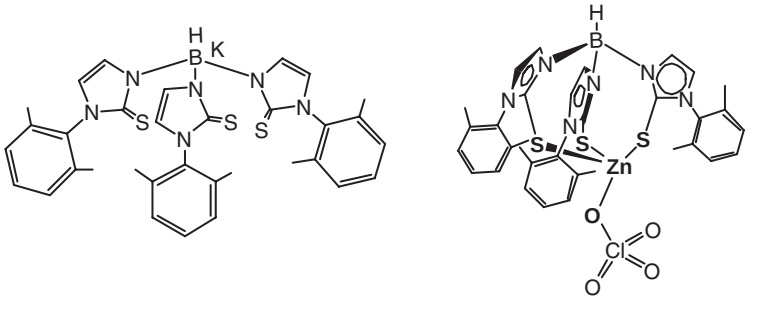
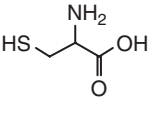


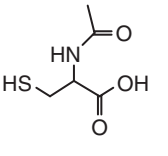
Scheme 1. Repair of damaged DNA by sacrificial alkylation of one of the zinc cysteine thiolate ligands of the N-Ada protein (*2*).

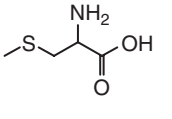
Herein, we continue our synthetic strategy to access zinc thiolate complexes, in which the zinc atoms are tetra-coordinated with the ligand Tt^{xylyl}, acting as S_3-tridentate and a changeable thiolate co-ligand such as cysteine, *N*-acetyl cysteine, and *S*-methyl cysteine (Scheme 2). The purpose



KTt^{xylyl} $[Tt^{xylyl}.Zn\text{-}OClO_3]$ **(1)**

$[Tt^{xylyl}.Zn\text{-}Cys\text{-}Zn\mathbf{Tt}^{xylyl}]$ (**2**) Cys= 

$[Tt^{xylyl}.Zn\text{-}Cys(NAc)\text{-}Zn\mathbf{Tt}^{xylyl}]$ (**3**) Cys(NAc)= 

$[Tt^{xylyl}.Zn\text{-}Cys(SMe)]$ (**4**) Cys(SMe)= 

Scheme 2. The structure of zinc(II) complex (*1*) and its thiolate derivatives.

is (i) to closely mimic the active site of *methionine* containing enzyme and (ii) to determine the effect of the steric and electronic nature of the bound thiolate co-ligand upon the rate of thiolate methylation.

Toward this end, three thiolate complexes containing cysteine and its derivatives [Tt^{xyly} · Zn-Cys-Zn · Tt^{xyly}] **2**, [Tt^{xyly} · Zn-Cys(NAc)-Zn · Tt^{xyly}] **3**, and [Tt^{xyly} · Zn-Cys(SMe)] **4** (Tt^{xyly} = hydrotris[*N*-xylyl-thioimidazolyl]borate, Cys = cysteine, Cys(SMe) = *S*-methyl cysteine, and Cys(NAc) = *N*-acetyl cysteine) (Scheme 2) were synthesized and characterized. The reactivity study of the zinc(II)-bound thiolate complex **2** as a structural model for the active site of *methionine synthase* toward methylation reactions was examined.

2. Results and discussion

2.1. *Characterization of the model complexes 1–4*

The zinc perchlorate complex [Tt^{xyly} · Zn-$OClO_3$] **1** was obtained by treating the $Zn(ClO_4)_2$ with an equivalent amount of the ligand KTt^{xyly} in methanol (*12*). The existence of complex **1** was proved by its structure determination. We had already shown that all kinds of thiols RSH react with Tt^{xylyl}Zn-$OClO_3$ **1** in the presence of a base such as sodium methoxide to form the corresponding Tt^{xylyl}Zn-SR species (*15*, *16*).

We designed and synthesized the zinc(II) thiolate complexes **2**, **3**, and **4** as structural models for the active site of *methionine synthase* (*3*), providing (i) tripodal ligands, which correspond to three cysteine amino acids, (ii) hydrophobic pockets, which specify the formation of tetrahedral zinc(II) units, and changeable thiolate co-ligands to achieve the formation of S_4Zn tetrahedral environment, as mentioned in Scheme 2. This is really the case shown by applying the reactions to the amino acid cysteine itself, first in in the unprotected form H_2Cys **2**, second in the protected form HCys(NAc) **3**, and third in the S-methylated cysteine **4**. In the first two dinuclear zinc(II)-containing thiolate complexes **2** and **3**, the carboxylate oxygen and the thiolate sulfur functions underwent reaction with the Zn-$OClO_3$ function. While the third monomeric zinc(II) complex **4**, the amino nitrogen and carboxylate oxygen functions underwent coordination.

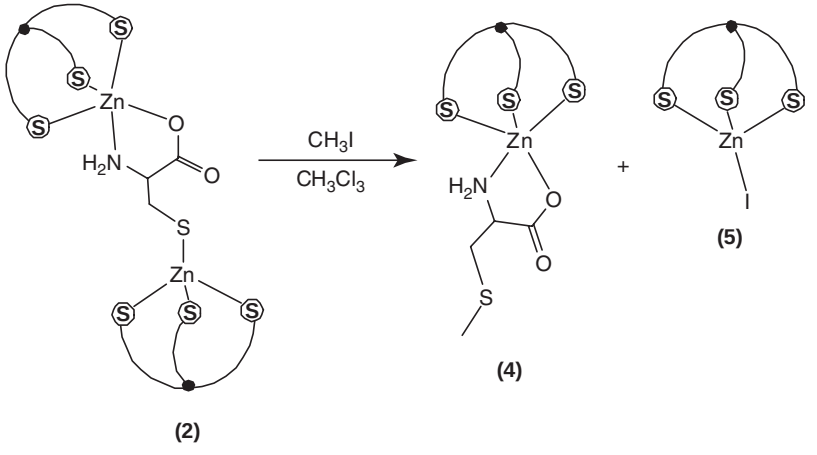
The electrical conductivity of complexes **2**–**4** in methanol were measured as a test of the degree of ionization of the complexes. The obtained results are 55, 49, and 51 Ωcm $mole^{-1}$, respectively (all at infinite dilution). These reduced conductivities indicate that the compounds are neutral and there are no ions outside the coordination sphere.

The thiolate function acts as a monodentate ligand yielding the usual symmetrical S_4Zn environment of the zinc ion in its Tt^{xyly} · Zn unit. It does not combine with the amino function to become a N,S chelate ligand like in the $Tp^{Cum,Me}$Zn-cysteine complex (*34*) because this would involve a six-membered chelate ring. Instead the amino function combines with the carboxylate function as a N,O chelate ligand, forming a five-membered chelate ring with the zinc ion of $Tp^{Me,Me}$Zn(HCys)Zn$Tp^{Me,Me}$ (*18*) and Tt^{xylyl}(HCys)ZnTp^{xylyl} (*16*) units. While this type of chelation is hithero unobserved in Tp*Zn chemistry, it is common in binary amino acid zinc complexes such as $Zn(Ala)_2$ (*35*) $Zn(Leu)_2$ (*36*) or Zn-$(Met)_2$ (*37*). Based on these results, the environment of the five-coordinate zinc ions in **2** and **3** may be described as distorted trigonal bipyramidal.

2.2. *Kinetic investigation for the methylation reactions*

The reaction of the dimeric zinc-bound functionalized thiolate complex **2** with CH_3I in chloroform results in the quantitative formation of the methylthioether [Tt^{xyly} · Zn-Cys(SMe)] **4** and the iodo

complex [Tt^{xyly} · Zn-I] **5** (*15*, *16*) as indicated in Scheme 3. The pseudo-first-order constants k_{obs} were calculated.



(2) **(4)** **(5)**

Scheme 3. The proposed mechanism for the methylation of (*2*) by using methyl iodide.

As we previously reported (*15*, *16*), the kinetic reaction was followed by ^{1}H-NMR spectroscopy in $CDCl_3$ at 300 K, and the increase in the intensities of methyl resonances of the produced methyl thioethers was recorded. Its proton chemical shifts are identical to those of the isolated methyl thioether [Tt^{xyly} · Zn-Cys(SMe)] **4**, indicating that the thioether product is not coordinated to zinc. A typical ^{1}H-NMR spectra for the methylation reaction between **2** and CH_3I in $CDCl_3$ as a representative example is shown in Figure 1. Under pseudo-first-order conditions, $[CH_3I]$ = ca. 15–40 [Tt^{xyly} · Zn-SR], the methylation exhibited first-order kinetics over at least five half lives. The reactions obeyed second-order rate law, *i.e.* first order in each reagent. ^{1}H-NMR intensities of the methyl protons of the produced methyl thioether, [Tt^{xyly} · Zn-Cys(SMe)] **4**, as a function of time for the reaction of **2** (10 mM) with CH_3I (50 mM) in $CDCl_3$ at 300 K are shown in Figure 2. According to Scheme 3, the methylation process is a second-order reaction. Its velocity is defined by Equation (1). When the concentration of CH_3I is in a large excess ($\geq$ 10-fold), the change of it can be neglected. The reaction rate is then expressed as in Equation (2):

$$\frac{-\mathrm{d}[\mathrm{Tt}^{xyly} \cdot \text{Zn-Cys-Zn} \cdot \mathrm{Tt}^{xyly}]}{\mathrm{dt}} = k\{[\mathrm{Tt}^{xyly} \cdot \text{Zn-Cys-Zn} \cdot \mathrm{Tt}^{xyly}]\}[CH_3I] \quad (1)$$

$$\frac{-\mathrm{d}[\mathrm{Tt}^{xyly} \cdot \text{Zn-Cys-Zn} \cdot \mathrm{Tt}^{xyly}]}{\mathrm{dt}} = k_{obs}[\mathrm{Tt}^{xyly} \cdot \text{Zn-Cys-Zn} \cdot \mathrm{Tt}^{xyly}], \quad (2)$$

where k_{obs} is the observed rate constant. During the reaction, when the decrease in the intenisities of the ^{1}H-NMR signals of the reactant thiolate complex [Tt^{xyly} · Zn-Cys-Zn · Tt^{xyly}] is recorded, Equation (3) is used for acquiring the first-order rate constant k_{obs}

$$\ln\{\mathrm{int}[\mathrm{Tt}^{xyly} \cdot \text{Zn-Cys-Zn} \cdot \mathrm{Tt}^{xyly}]_t\} = -k_{obs}t, \quad (3)$$

while in the case of recording the increase in the intensities of ^{1}H-NMR signals of the produced methyl thioether [Tt^{xyly} · Zn-Cys(SMe)], Equation (4) is used. where a is a changeable constant depending on the reactant thiolate complex **2** and the produced thioether [Tt^{xyly} · Zn-Cys(SMe)] ($a = N_c/N_r\ N_o$, where N_c is the reactant proton number of complex **2**, N_r is the total proton number of **2**, and N_o is the observed proton number). From the [Tt^{xyly} · Zn-Cys(SMe)] signal

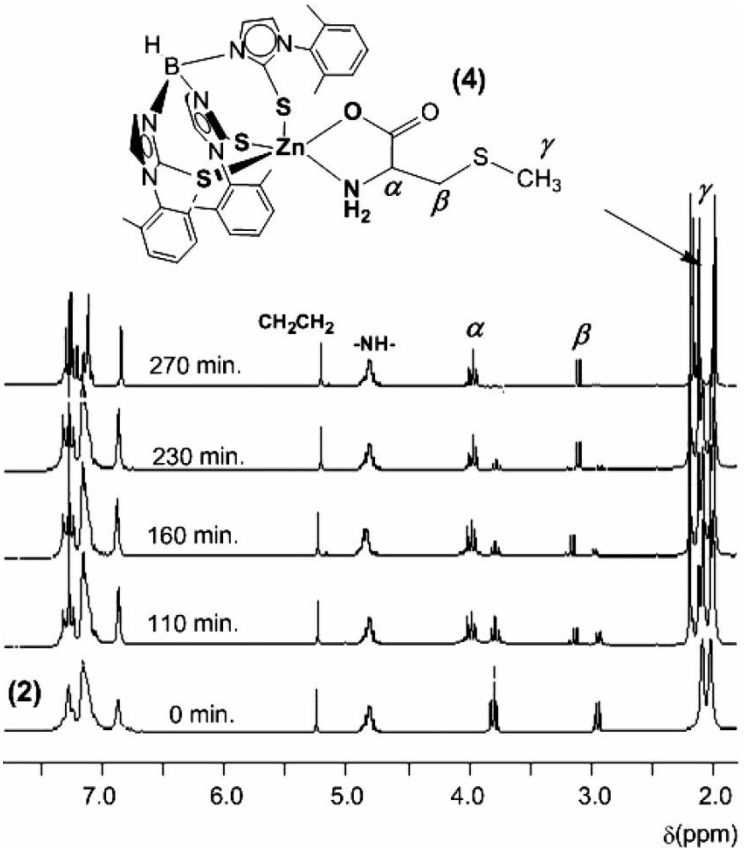


Figure 1. ^{1}H-NMR spectra for the reaction of [Tt^{xylx}·Zn-Cys-Zn·Tt^{xylx}] **2** (10 mM) with CH_3I (50 mM) in $CDCl_3$ at 300 K as a function of time.

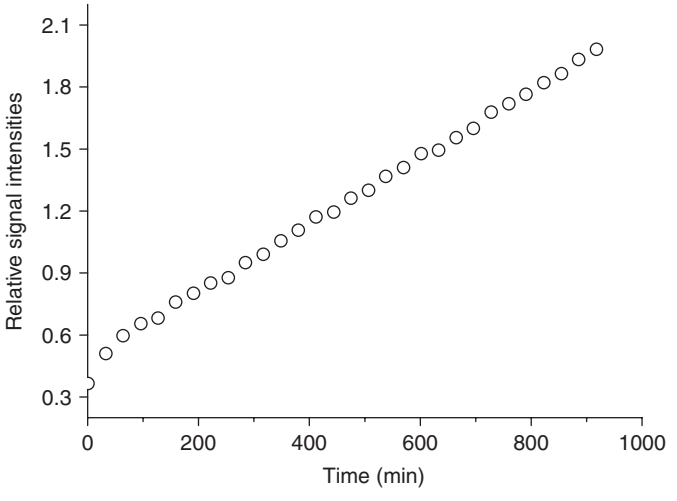


Figure 2. ^{1}H-NMR intensities of the methyl protons of [Tt^{xylx}·Zn-Cys(SMe)] as a function of time for the reaction of [Tt^{xylx}·Zn-Cys-Zn·Tt^{xylx}] **2** (10 mM) with CH_3I (50 mM) in $CDCl_3$ at 300 K.

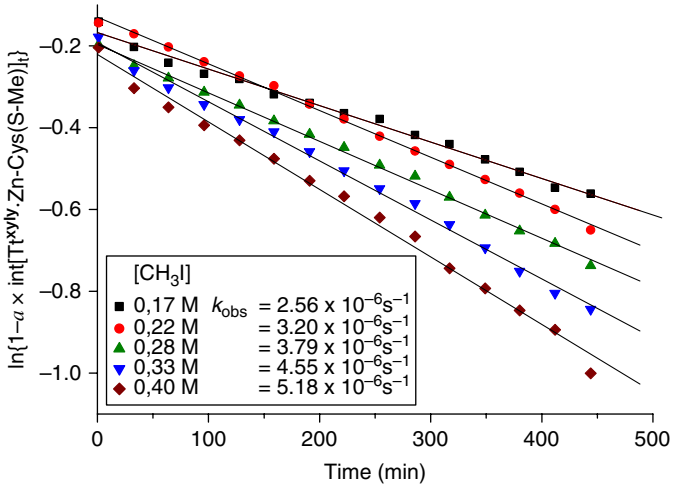


Figure 3. Semi-logarithmic plot for the methylation of [Tt^{xyly}·Zn-Cys-Zn·Tt^{xyly}] **2** (10 mM) by using CH_3I (50 mM) in $CDCl_3$ at 300 K.

intensities, recorded for at least five $t_{1/2}$ intervals (Figure 2), the pseudo-first-order rate constants were obtained according to Equation (5):

$$\ln\{1 - a \times \text{int}[Tt^{xyly} \cdot \text{Zn-Cys(SMe)}]_t\} = -k_{obs}t \quad (4)$$

$$k_{obs} = k[CH_3I]. \quad (5)$$

The semi-logarithmic plot for the methylation of **2** at five different excess concentrations of CH_3I are linear with correlation coefficients >0.995 (Figure 3). The second-order rate constants, obtained according to $k_{obs} = k[CH_3I]$, was found to be $1.0 \times 10^{-5}\,M^{-1}\,s^{-1}$.

The rate constant observed here for the methylation of complex **2** with methyl iodide is much lower than other neutral zinc thiolte complexes [Tt^{xyly} · Zn-SR] (R = ethyl, benzyl, and phenyl) (*16*) and also lower than those containing functional groups. For example, Parkin (*4*), Riordan and coworkers (*32*, *33*), Carrano and coworkers (*28*), and we (*7*, *16*) reported rates of 1.3×10^{-4}, ca. 1.2×10^{-4}, and $5.96 \times 10^{-5}\,M^{-1}\,s^{-1}$ for methyl iodide reaction to [Ph(Pz^{tBu})]Zn-SC_6H_4-o-NHC(O)-*t*Bu), [L1O]Zn(SC_6H_4-*o*-NHC(O)Me), and [Tt^{xyly} · Zn-SC_6H_4-*o*-CH_2OH]], respectively. This difference in reactivity indicates that the steric hindrance around the thiolate sulfur provided a quantitative assessment in altering its reactivity. Most of these enzymes have a sulfur-rich coordination of zinc. It suggests that the coordination of zinc by sulfur donors is the most efficient way to increase its electron density and hence the nucleophilicity of the zinc-bound thiolate coligands (*15*, *16*).

3. Conclusion

This paper has shown that the essential steps and key intermediates of thiolate alkylations by zinc enzymes, specifically the action of *methionine synthase*, can be modeled by thioimidazolylborate-zinc complexes. Three thiolate complexes-containing cysteine and its derivatives [Tt^{xyly} · Zn-Cys-Zn · Tt^{xyly}] **2**, [Tt^{xyly} · Zn-Cys(NAc)-Zn · Tt^{xyly}] **3**, and [Tt^{xyly} · Zn-Cys(SMe)] **4** were synthesized and characterized. Methylation of the coordinated thiolate in the dinuclear zinc(II) complex **2** with methyl iodide appears to occur intramolecularly at the zinc-bound thiolates.

The major pieces of evidence are (i) the occurrence of the alkylations in completely nonpolar media and (ii) the clean second-order kinetics for the methylation of **2** by methyl iodide.

4. Experimental

4.1. *General data*

All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods. The IR absorption spectra were recorded using FT-IR Prestige-21 Shimadzu apparatus, in the range of 400–4000 cm^{-1}. ^{1}H-NMR spectra were measured on a JEOL EX-400 instrument. The chemical shifts are reported relative to the resonance signal of tetramethylsilane (TMS), which is used as an internal standard. The conductivity measurements were carried out using Equiptronics digital conductivity meter model JENWAY 4070 type at room temperature for (1×10^{-3} M) solutions. The ligand potassium hydrotris[*N*-xylyl-2-thioimidazolyl]borate KTt^{xyly} and its zinc(II)-bound perchlorate complex **1** were prepared according to the published procedures (*11*). The sodium salts of cysteine and its derivative were prepared in *situ* from the reaction with 0.25 M stock solution of sodium methoxide.

4.2. *Syntheses*

4.2.1. *Synthesis of* [$Tt^{xyly} \cdot Zn\text{-}Cys\text{-}Zn\ Tt^{xyly}$] ***2***

The sodium salt of L-cysteine was prepared by combining 73 mg (0.60 mmol) L-cysteine and 2.4 ml (0.60 mmol) of the NaOMe stock solution in 15 ml of methanol. This solution was added dropwise to a solution of 448 mg (1.2 mmol) $Zn(ClO_4)_2{\cdot}6H_2O$ and 792 mg (1.2 mmol) KTt^{xyly} in 35 ml of methanol. After 3 days of stirring, the solution was evaporated to dryness. The residue was extracted with 20 ml of dichloromethane, filtered, and evaporated to dryness again. Crystallization was from methanol/dichloromethane. Yield 95 mg (53); m.p. 201°C. Anal. for $C_{69}H_{73}B_2N_{13}O_2S_7Zn_2$ (1492.22). Calcd: C, 55.49; H, 4.93; N, 12.20; S, 15.00; Zn, 8.76. Found: C, 55.01; H, 4.99; N, 12.02; S, 14.89, Zn, 8.75. IR (KBr): 3364 (br, NH), 2438 (B−H), 1656 (s, CO), 1603 cm^{-1} (s, CO). ^{1}H-NMR ($CDCl_3$, 298 K, TMS): $\delta = 1.92$ (s, 18H, Me), 2.01 (s, 18H, Me), 2.93 (d, $J = 2.0$ Hz, 2H, $-S-CH_2^{\beta}-$), 3.81 (t, $J = 7.2$ Hz, 1H, $-CH^{\alpha}-$), 4.74 (br, 1H, NH), 6.77 (d, $J = 2.4$ Hz, 6H, Im), 7.01 (m, 12H, Ph (3,5)), 7.05 (d, $J = 2.4$ Hz, 6H, Im), 7.17 (t, $J = 7.2$ Hz, 6H, Ph (4)) ppm.

4.2.2. *Synthesis of* [$Tt^{xyly} \cdot Zn\text{-}Cys(NAc)\text{-}Zn\ Tt^{xyly}$] ***3***

The sodium salt of *N*-acetylcysteine was prepared by combining 98 mg (0.60 mmol) *N*-acetylcysteine and 2.4 ml (0.60 mmol) of the NaOMe stock solution in 15 ml of methanol. This solution was added dropwise to a solution of 448 mg (1.2 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$ and 792 mg (1.2 mmol) KTt^{xyly} in 35 ml of methanol. After 3 days of stirring, the solution was evaporated to dryness. The residue was extracted with 20 ml of dichloromethane, filtered, and evaporated to dryness again. Crystallization was from methanol/dichloromethane. Yield 84 mg (46%); m.p. 204°C. Anal. for $C_{72}H_{78}B_2N_{13}O_4S_7Zn_2 + CH_3OH$ (1531.21 + 32.03). Calcd.: C, 55.20; H, 5.02; N, 11.63; S, 14.30; Zn, 8.35. Found: C, 54.37; H, 5.01; N, 11.75; S, 14.44, Zn, 8.53. IR (KBr): 3355 (br, NH), 2429 (B−H), 1650 (s, CO), 1611 cm^{-1} (s, CO). ^{1}H-NMR ($CDCl_3$, 298 K, TMS): $\delta = 1.71$ (s, 3H, $CH_3-C(O)-$), 1.90 (s, 18H, Me), 1.98 (s, 18H, Me), 2.89 (d, $J = 2.2$ Hz, 2H, $-S-CH_2^{\beta}-$), 3.80 (t, $J = 7.2$ Hz, 1H, $-CH^{\alpha}-$), 4.23 (br, 1H, NH), 6.76 (d, $J = 2.2$ Hz, 6H, Im), 6.99 (m, 12H, Ph (3,5)), 7.03 (d, $J = 2.2$ Hz, 6H, Im), 7.19 (t, $J = 7.5$ Hz, 6H, Ph (4)) ppm.

4.2.3. *Synthesis of* $[Tt^{xyly} \cdot Zn\text{-}Cys(SMe)]$ ***4***

The sodium salt of *S*-methylcysteine was prepared by combining 81 mg (0.60 mmol) *S*-methylcysteine and 2.4 ml (0.60 mmol) of the NaOMe stock solution in 15 ml of methanol. This solution was added dropwise to a solution of 224 mg (0.6 mmol) $Zn(ClO_4)_2{\cdot}6H_2O$ and 396 mg (0.6 mmol) of KTt^{xyly} in 20 ml of methanol. After 4 days of stirring, the solution was evaporated to dryness. The residue was extracted with 20 ml of dichloromethane, filtered, and evaporated to dryness again. Crystallization was from methanol/dichloromethane. Yield 92 mg (59%); m.p. 204°C. Anal. for $C_{37}H_{43}BN_7O_2S_4Zn + CH_3OH$ (821.64 + 32.03). Calcd.: C, 53.42; H, 5.55; N, 11.48; S, 14.98; Zn, 7.43. Found: C, 53.37; H, 5.58; N, 11.65; S, 14.10, Zn, 7.19. IR (KBr): 3369 (br, NH), 2433 (B−H), 1651 cm^{-1} (CO). ^{1}H-NMR ($CDCl_3$, 298 K, TMS): $\delta = 1.91$ (s, 9H, Me), 2.00 (s, 9H, Me), 2.12 (s, 3H, $S{-}CH_3^{\gamma}$), 3.21 (d, $J = 2.0$ Hz, 2H, $-S{-}CH_2^{\beta}-$), 4.11 (t, $J = 7.2$ Hz, 1H, $-CH^{\alpha}-$), 4.69 (br, 1H, NH), 6.78 (d, $J = 2.0$ Hz, 3H, Im), 7.00 (m, 6H, Ph (3,5)), 7.04 (d, $J = 2.0$ Hz, 3H, Im), 7.17 (t, $J = 7.0$ Hz, 3H, Ph (4)) ppm.

4.3. *Kinetic measurements for the reaction of the model complex 2 with* CH_3I

All experiments were performed under pseudo-first-order conditions with large excess of methyl iodide. In a typical experiment, In a typical experiment: 100 µl (0.01 M) of the thiolate complex in $CDCl_3$ (99.8%) is placed in an NMR tube followed by the immediate addition of different concentrations of MeI (0.17, 0.22, 0.28, 0.33, and 0.40 M, respectively). All the reactions were monitored by ^{1}H-NMR spectroscopy at 300 K. The ^{1}H-NMR signals of the three thioimidazolyl protons of the reactant thiolate complex **2** (*15*, *16*) were used as an integral standard. The increase in the intensity of the methyl protons of the produced methylthioether $[Tt^{xyly} \cdot Zn\text{-}Cys(SMe)]$ **4** were recorded and integrated relative to the standard thioimidazole protons. Typical ^{1}H-NMR parameters for the kinetic studies included 16 scans per spectrum and five spectra per reaction. Each kinetic run was made triplicate. The averaged data were used for calculations.

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