

Syntheses, Reactivity, and Molecular Structures of *RSRS*-[Ni(tmc)SC₆H₅](PF₆), *RRSS*-[Ni(tmc)SC₆H₅](CF₃SO₃), and *RRSS*-[Ni(tmc)](CF₃SO₃) (tmc = 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane)

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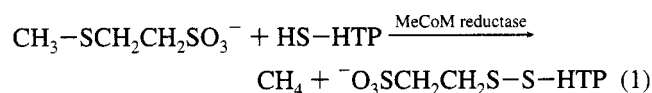
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The *RSRS* and *RRSS* isomers of [Ni(tmc)](OTf)₂ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; OTf[−] = CF₃SO₃[−]) react with NaSC₆H₅ to yield the corresponding high spin, five-coordinate derivatives, [Ni(tmc)SC₆H₅](OTf). The molecular structure of each has been determined by X-ray diffraction. *RRSS*-[Ni(tmc)SC₆H₅](OTf) crystallized in the monoclinic space group *P*2₁/*n*, with *a* = 12.648(3) Å, *b* = 15.145(4) Å, *c* = 14.765(4) Å, β = 113.96(2)°, *V* = 2584(1) Å³, and *Z* = 4. The coordination sphere about Ni is best described as square pyramidal with a Ni–S bond distance of 2.369(2) Å and Ni–N_{av} of 2.128 Å. *RSRS*-[Ni(tmc)SC₆H₅](PF₆) crystallized in the monoclinic space group *P*2₁/*n*, with *a* = 13.037(5) Å, *b* = 15.407(7) Å, *c* = 13.706(7) Å, β = 113.53(3)°, *V* = 2524(2) Å³, and *Z* = 4. The Ni resides in a highly distorted square pyramid with a shorter Ni–S distance, 2.352(2) Å and correspondingly longer Ni–N_{av} distance of 2.149 Å. Alternatively [Ni(tmc)SR](OTf) may be produced by oxidative addition of disulfide, R₂S₂ (R = C₆H₅, C₂H₅), to Ni(tmc)(OTf). The second-order rate constant, *k*₁, for reaction with (C₆H₅)₂S₂ is 120 M^{−1}s^{−1}. (C₂H₅)₂S₂ reacts 5 orders of magnitude more slowly consistent with its greater S–S bond dissociation energy. The nickel thiolates react with haloalkanes, RX (RX = CH₃I, C₂H₅I, (CH₃)₂CHI, C₆H₅CH₂Cl), producing [Ni(tmc)X](OTf) and C₆H₅SR. The reaction is second order with *k*₂ decreasing in the order, CH₃I > C₂H₅I > (CH₃)₂CHI. Strikingly, for reactions with a given RX, the *RRSS* isomer reacted *ca.* 350 times faster than the *RSRS* isomer. *RRSS*-[Ni(tmc)](OTf)·Na(OTf) has also been characterized, having crystallized in the monoclinic space group *C*2/*c*, with *a* = 24.690(13) Å, *b* = 11.261(5) Å, *c* = 9.681(6) Å, β = 91.03(4)°, *V* = 2691(2) Å³, and *Z* = 4. The macrocycle provides the Ni(I) ion with a square planar coordination environment in which there are two distinct Ni–N bond distances, 2.120(5) and 2.095(5) Å.

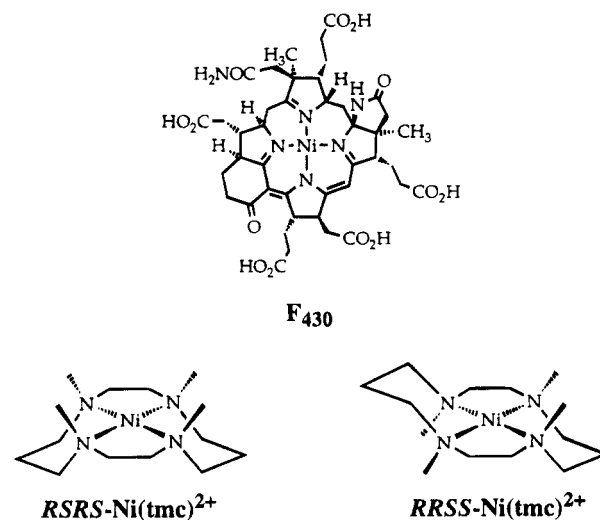
Introduction

F₄₃₀ is the nickel-containing prosthetic group of methyl coenzyme M reductase which, in the final step of methanogenesis, catalyzes the reductive cleavage of methyl coenzyme M (MeCoM)¹ in the presence of a thiol cofactor to produce methane and a mixed disulfide, eq 1.² The enzyme also appears



to be involved in the reductive dehalogenation of chlorinated hydrocarbons by methanogenic bacteria.³ The structure of F₄₃₀ has been established (Chart 1) and the nickel appears to be redox active cycling between Ni(II) and Ni(I) during catalysis.⁴ While

Chart 1



the specific mechanism by which the enzyme catalyzes C–S bond rupture remains unclear, the Ni(I) state of *isolated* F₄₃₀ does not react directly with organosulfides including MeCoM.⁵

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- (1) Abbreviations: MeCoM, CH₃SCCH₂CH₂SO₃[−]; HS–HTP, (7-mercaptoheptanoyl)threonine phosphate; dioxo[16]aneN₅, 1,4,7,10,13-pentaaazacyclohexadecane-14,16-dione; tmc, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; OTf[−], CF₃SO₃[−]; Me₁₀[14]aneN₄, 1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane; tc1, 8-methyl-1,3,6,8,10,13,15-heptaazatricyclo[13.1.1.1^{13,15}]octadecane; tc2, 1,3,6,9-11,14-hexaazamacrotricyclo[12.2.1.1^{6,9}]octadecane; htim, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradecane; diene, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetra-4,11-diene; OEP, 2,3,7,8,12,12,17,18-octaethylporphyrinato dianion; [14]ane-N₄, 1,4,8,11-tetraazacyclotetradecane.

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Ni(I)-F₄₃₀ does react with CH₃I to produce methane via a Ni-CH₃ intermediate.⁵ While these results have motivated model studies aimed at elucidating mechanistic parameters for the activation of MeCoM,⁶ only one system, Ni(dioxo[16]aneN₅),^{6a} liberates stoichiometric quantities of methane from MeCoM. However, the oxidative nature of this system seems incompatible with our current knowledge of F₄₃₀.

To further our understanding of the F₄₃₀-catalyzed system, we have examined reactions of organosulfides, thiols and disulfides with [Ni(tmc)](OTf)₂ and [Ni(tmc)](OTf). [Ni(tmc)](OTf)₂ exists predominantly as two isomers, *RSRS* and *RRSS* (Chart 1).⁷ These may be prepared by alternate synthetic routes and they do not equilibrate in solution at room temperature.⁸ The tmc ligand was chosen as a model for F₄₃₀ based on the following criteria. (1) As the Ni(II)/Ni(I) redox couple appears to be involved in the catalytic reduction of MeCoM by F₄₃₀, we sought a N₄ macrocycle which would stabilize these oxidation states to a similar extent as F₄₃₀. The redox couples for Ni(tmc)^{2+/+}, $E_{1/2} = -0.780$ V (CH₃CN, vs Ag/AgCl) for the *RSRS* isomer and -0.960 V for the *RRSS* isomer,⁹ are very close to the redox couple for F_{430M} (the pentamethylester of F₄₃₀), $E_{1/2} = -0.748$ V.¹⁰ Therefore, the reducing potential of [Ni(tmc)](OTf) mirrors that of F_{430M}. (2) Several researchers have invoked a Ni-CH₃ intermediate during methyl coenzyme M reductase catalysis.^{2d,e} Perhaps consistent with this proposal low temperature alkylation of Ni(I)-F_{430M} with CH₃I or (CH₃)₃S⁺ results in formation of a Ni-CH₃ intermediate.⁵ Subsequent hydrolysis of the Ni-CH₃ bond produces methane. [Ni(tmc)](OTf) may also be alkylated to yield an isolable Ni-CH₃ species.^{9b,11} (3) The tmc ligand is sufficiently flexible to permit binding of exogenous ligands in axial coordination sites. In acetonitrile, *RSRS*-[Ni(tmc)](OTf)₂ exists as a five-coordinate, square pyramidal complex solvated with one CH₃CN.¹² *RRSS*-[Ni(tmc)](OTf)₂ binds two CH₃CN to form a six-coordinate

species. Notably, both F_{430M} and [Ni(tmc)](OTf)₂ bind imidazole strongly, the former yielding a six-coordinate adduct.¹³

Herein we report the syntheses, characterization and reactivity patterns of *RSRS*-[Ni(tmc)SC₆H₅](OTf) and *RRSS*-[Ni(tmc)-SC₆H₅](OTf), accessible by several synthetic routes, including oxidative addition of (C₆H₅)₂S₂ to [Ni(tmc)](OTf). This represents the first structural account of five-coordinate complexes of both the *RSRS* and *RRSS* isomers. As such it permits comparison of relevant metric parameters. Solid state structural differences are reflected in the rates of alkylation of [Ni(tmc)-SC₆H₅](OTf) with haloalkanes. During the course of this study, we have crystallographically characterized *RRSS*-[Ni(tmc)](OTf), a structural model for the reduced form of F₄₃₀.

Experimental Section

Materials and Methods. All reagents were distilled under N₂ and dried as indicated. THF, Et₂O, and benzene were freshly distilled over Na/benzophenone. Acetonitrile was distilled over CaH₂ and collected after discarding the first fraction. Haloalkanes were distilled over CaH₂ at reduced pressures under N₂ and were stored protected from light over Cu wire. (C₆H₅)₂S₂ was distilled under reduced pressure. (C₆H₅)₂S₂ was used as received. Elemental analyses were performed by Desert Analytics and Schwarzkopf Microanalytical, Inc. Electronic spectra were recorded with a SLM-Aminco 3000 diode array spectrophotometer. NMR spectra were recorded on a 400 MHz Bruker spectrometer equipped with a Sun workstation. GC-MS were performed on a Hewlett-Packard 5989A mass spectrometer equipped with a HP 5890-II gas chromatograph. Kinetic experiments were monitored by UV-visible spectroscopy in cuvettes which were temperature regulated in a thermostated cell holder equilibrated with a circulating bath. Cyclic voltammetry was performed on a BAS 50W voltammetric analyzer. Experiments were performed in an Ar-filled glovebox in a cell consisting of a glassy carbon working electrode (1 mm), Pt wire counter electrode and Ag/AgCl reference electrode. Solutions contained 0.1 M electrolyte ([Bu₄N][PF₆]) and 2–5 mM sample. Potentials were referenced to internal Fc/Fc⁺ (+410 mV vs Ag/AgCl). *RRSS* and *RSRS*-[Ni(tmc)](OTf)₂ were prepared according to Barefield.¹⁴ The corresponding PF₆⁻ salts were obtained from the triflates by precipitation from water upon addition of aqueous [NH₄][PF₆]. The isomeric purity of the nickel(II) complexes was determined by their aqueous electronic spectra, $\lambda_{\max}$, nm (ϵ , M⁻¹ cm⁻¹): *RSRS*, 395 (103), 514 (66), 654 (30); *RRSS*, 494 (27), 367 (10). In general, the *RRSS* derivatives were found to be less soluble than the *RSRS* species. NaSC₆H₅ was prepared by addition of C₆H₅SH (2.0 g, 18 mmol) to Na metal (600 mg, 26 mmol) in 30 mL THF. NaSC₆H₅ precipitated as a white powder, was dried under reduced pressure at 60 °C for 12 h and stored in the glovebox. The salt was extremely hygroscopic.

[Bu₄N][MeCoM]. [Na][MeCoM] was prepared according to Wolfe.¹⁵ The Bu₄N⁺ salt could not be prepared by simple solution metathesis with [Bu₄N]Cl. The cation exchange resin Sephadex SP-C-25 was converted to the acid by treatment with CF₃SO₃H. The acid form of the exchange resin was treated with [Bu₄N]OH and washed with water several times to obtain the Bu₄N⁺ exchange resin. An aqueous solution of [Na][MeCoM] was passed through the exchange resin and the resulting solution was rotary evaporated to dryness. [Bu₄N][MeCoM]: ¹H NMR (D₂O) δ 3.27 (t, CH₂SO₃, 2 H), 3.23 (m, NCH₂, 8 H), 2.95 (t, SCH₂, 2 H), 2.21 (s, SCH₃, 3 H), 1.70 (m, CH₂, 8 H), 1.40 (m, CH₂, 8 H), 1.00 (t, CH₃, 12 H). Although [Bu₄N][MeCoM] was soluble in organic solvents, it precipitated in the presence of [Ni(tmc)](OTf) even in Me₂SO. [Bu₄N][MeCoM] did not precipitate upon addition of [Ni(tmc)](OTf)₂.

***RRSS*-[Ni(tmc)](OTf)·Na(OTf).** [Ni(tmc)](OTf)₂ (either isomer) (1.0 g, 1.6 mmol) was stirred with 50 g of Na/Hg (0.3%) in 22 mL of

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THF-CH₃CN (10:1). After 30 min, the solution was filtered and the product precipitated by addition of Et₂O and hexanes. Recrystallization from THF-Et₂O yielded blue-green crystals of [Ni(tmc)](OTf) cocrystallized with NaOTf in greater than 90% yield. Electronic spectrum (THF): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹) 351 nm (4000). Anal. Calcd for C₁₆H₃₂F₆N₄NaNiO₆S₂: C, 30.20; H, 5.03; N, 8.89. Found: C, 30.04; H, 4.99; N, 8.51. [Ni(tmc)](OTf) was extremely O₂ sensitive, turning readily to red upon exposure to air.

RSRS-[Ni(tmc)SC₆H₅](PF₆). Addition of NaSC₆H₅ (35 mg, 0.27 mmol) to a THF slurry of RSRS-[Ni(tmc)](PF₆)₂ (170 mg, 0.28 mmol) resulted in an immediate change from a purple suspension to a deep orange solution. After 5 min, the solution was filtered and the product precipitated by addition of Et₂O and hexanes. Isolated yield: 120 mg (80%). Electronic spectrum (THF), λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 475 nm (3000), 341 nm (2330). Anal. Calcd for C₂₀H₃₇F₆N₄NiPS: C, 42.17; H, 6.50; N, 9.84. Found: C, 42.41; H, 6.52; N, 9.71. In solution, this isomer lost tmc readily in the presence of trace moisture. X-ray quality crystals were grown by diffusing Et₂O into a concentrated THF-hexanes (90:10) solution.

RRSS-[Ni(tmc)SC₆H₅](PF₆). This complex was prepared similarly to the RSRS isomer, except THF-CH₃CN (4:1) replaced neat THF as solvent, owing to the poorer solubility of this isomer in THF. Isolated yield: 90 mg (60%). Electronic spectrum (THF), λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 469 nm (3000), 362 nm (2220). Anal. Calcd for C₂₀H₃₇F₆N₄NiPS: C, 42.17; H, 6.50; N, 9.84. Found: C, 42.25; H, 6.38; N, 10.02. The more soluble triflate salts of both RSRS- and RRSS-[Ni(tmc)-SC₆H₅]⁺ were prepared in an analogous manner and had identical electronic spectral features. X-ray quality crystals of the OTf⁻ salt were grown by slowly cooling a concentrated THF-hexanes (90:10) solution to -35 °C.

Spectral Titrations. Titrations were performed in acetone because the RRSS- and RSRS-[Ni(tmc)](OTf)₂ complexes are four coordinate in this solvent as indicated by the presence of only the 514 nm band in the visible spectra. Addition of potential ligands Me₂SO, CH₃CN, RSCH₃ (R = CH₃, C₂H₅), NaSC₆H₅, to RSRS-[Ni(tmc)](OTf)₂ (15 mM) resulted in diminution of the 514 nm feature with concomitant appearance of two new bands at 394 nm and 650 nm. Titrations were continued until addition of subsequent aliquots of ligand produced no further spectral changes. The number of exogenous ligands bound (slopes) and binding constants (γ -intercepts) were determined from linear plots of $\ln[(A - A_0/A_\infty - A)]$ vs $\ln[\text{ligand}]$. In cases where the binding was strong, K was estimated relative to that of CH₃CN as exemplified by SC₆H₅⁻ ligation. For SC₆H₅⁻ binding in CH₃CN, $K^{\text{SC}_6\text{H}_5}/K_1[\text{CH}_3\text{CN}] = [\text{Ni}(\text{tmc})\text{SC}_6\text{H}_5(\text{OTf})]/[\text{Ni}(\text{tmc})(\text{NCCH}_3)(\text{OTf})_2]$. At $[\text{Ni}(\text{tmc})\text{SC}_6\text{H}_5(\text{OTf})] = 2 \text{ mM}$, $[\text{CH}_3\text{CN}] = 20 \text{ M}$, binding was complete as measured by UV-visible spectroscopy ($[\text{Ni}(\text{tmc})\text{SC}_6\text{H}_5(\text{OTf})]/[\text{Ni}(\text{tmc})(\text{NCCH}_3)(\text{OTf})_2] > 10$), which sets a lower limit on $K^{\text{SC}_6\text{H}_5}$ of 10⁵ M⁻¹. Similar analysis with I⁻ competing with SC₆H₅⁻ yielded $K^{\text{SC}_6\text{H}_5} > 10^6 \text{ M}^{-1}$.

Cyclic Voltammetric Measurements. The equilibrium binding constant for SC₆H₅⁻, $K^{\text{SC}_6\text{H}_5}$, was measured independently by an electrochemical method. In the presence of 1 equiv of NaSC₆H₅, the Ni(II/I) redox potential of [Ni(tmc)](OTf)₂ shifted to -0.95 V (CH₃CN, vs Ag/AgCl). Since Ni(I) does not bind exogenous ligands, the shift in potential reflects Ni(II) binding SC₆H₅⁻. Applying the Nernst equation yields a lower limit for $K^{\text{SC}_6\text{H}_5}$ of 10⁶ M⁻¹. Further addition of NaSC₆H₅ was not possible due to significant precipitation and decomposition. Therefore, we were left with only a lower limit for the binding constant. However, this value agrees with that measured spectrophotometrically. The cyclic voltammetry method yielded identical $K^{\text{SC}_6\text{H}_5}$ values for both RSRS- and RRSS-[Ni(tmc)](OTf)₂.

Product Analysis. Production of thioanisole, C₆H₅SC₂H₅, from reactions of RSRS- and RRSS-[Ni(tmc)SC₆H₅](OTf) with CH₃I was confirmed by GC-MS analysis. In a typical experiment, 2 equiv of CH₃I (20 mM) was added to [Ni(tmc)SC₆H₅](OTf) (10 mM) in THF. After 12 h, 0.5 μ L aliquots were injected onto a RTX-5 column. The column temperature was programmed as follows: 70 °C for 1 min and then ramping at 20 °C/min to 200 °C. Thioanisole production was determined by its characteristic retention time, 4.86 min, and mass spectral features, (M^+ , m/e 124). These data were identical with those of an authentic sample of thioanisole. Yields were greater than 90%.

Kinetics. [Ni(tmc)](OTf) + (C₂H₅)₂S₂. THF solutions of [Ni(tmc)](OTf) were prepared in a spectrophotometric cell inside a Ar-filled glovebox. Reactions were initiated by injecting neat Et₂S₂ into thermostated Ni(I) solutions through a septum-capped sidearm. Rates were measured by monitoring absorbance increases at 414 nm (λ_{max} for [Ni(tmc)SC₂H₅](OTf)) or absorbance decreases at 351 nm (λ_{max} for [Ni(tmc)](OTf)). Values of k_{obs} were obtained from the slope of plots of $\ln(A - A_\infty)$ vs time which were linear over 3 half-lives. A plot of k_{obs} vs [(C₂H₅)₂S₂] was also linear, confirming the first order dependence on [(C₂H₅)₂S₂].

[Ni(tmc)](OTf) + (C₆H₅)₂S₂. This reaction was too rapid to monitor by conventional spectrophotometric methods even under high dilution. However, an estimate of k_{obs} was obtained from the second half of the reaction under second order conditions: [[Ni(tmc)](OTf)] = 2 mM, [(C₆H₅)₂S₂] = 1 mM, $t_{1/2}$ = 8 s. These data yielded a crude estimate for the second-order rate constant of approximately 120 M⁻¹ s⁻¹. A more accurate determination of the rate constant was obtained by cyclic voltammetry.¹⁶ In CH₃CN, with [Bu₄N][PF₆] (0.1 M) as supporting electrolyte, the cyclic voltammograms of [Ni(tmc)](OTf)₂ (2.5 mM) were obtained in the presence of 0, 10, 20, 44, and 91 mM (C₆H₅)₂S₂. The scan rate for each [(C₆H₅)₂S₂] was varied: 50, 100, 200, 500, 1000, and 2000 mV/s. E_f for [Ni(tmc)](OTf)₂ was at -0.78 V. The cathodic and anodic currents were measured and corrected for background currents. Thus τ = 220 mV/scan rate, where τ is defined as the time required to scan from the formal potential to the switching potential (-1.0 V) and the scan rate is the estimated scan rate at which $i_a = i_c/2$.¹⁶ The pseudo first order rate constant, k_{obs} , is the inverse of τ under these conditions. A linear plot of k_{obs} vs [(C₆H₅)₂S₂] yielded the second-order rate constant of 120 M⁻¹ s⁻¹. It should be noted that this method of obtaining rate constants from current ratios provides only an estimate and not a precise rate constant compared to other electrochemical or spectral methods. This approach was applied to RSRS-[Ni(tmc)](OTf)₂ in CH₃CN but could not be applied to the RRSS isomer because its reduction interfered severely with the direct electrochemical reduction of (C₆H₅)₂S₂ in CH₃CN.

[Ni(tmc)SC₆H₅](OTf) + RX. Stock solutions of [Ni(tmc)-SC₆H₅](OTf) in THF-CH₃CN (1:1)¹⁷ were prepared in a Ar-filled glovebox. Aliquots (0.5–1.0 mM) were transferred to a 1 cm quartz spectrophotometric cell which was sealed under Ar with a Kontes roto-seal tap. Reactions were initiated by injecting the appropriate amount of haloalkane through a septum-capped sidearm. Rates were measured by monitoring absorbance changes at 463 nm (occasionally at 485 nm) corresponding to the disappearance of [Ni(tmc)SC₆H₅](OTf). Values of k_{obs} were obtained from the slope of plots of $\ln(A - A_\infty)$ vs time which were linear over three half-lives. Plots of k_{obs} vs [RX] were also linear, confirming the first order dependence on [RX]. In two cases where the reactions were slowest, (CH₃)₂CHI and C₆H₅CH₂Cl reacting with RSRS-[Ni(tmc)SC₆H₅](OTf), there were significant deviations from pseudo-first-order behavior. In these instances, the initial 10% of the data were in accord with pseudo-first-order behavior, while deviations in the latter data were consistent with competitive Ni-SC₆H₅ bond rupture followed by fast alkylation of SC₆H₅⁻ in solution.

Crystallographic Structural Determinations. Crystallographic data for the structures are collected in Table 1 and in the Supporting Information. Specimens were mounted on glass fibers and found photographically to possess 2/*m* Laue symmetry. Systematic absences in the diffraction allowed unique assignments of space groups. The data sets were semiempirically corrected for absorption and solved by heavy-atom methods. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were idealized. All computations used SHELXTL-PC software (Ver. 4.2, G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

Organic Sulfide Binding to Ni(tmc)(OTf)₂. RSRS- and RRSS-[Ni(tmc)](OTf)₂ react cleanly with organic sulfides, RSR⁻,

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(17) This solvent mixture was necessary because (i) RRSS-[Ni(tmc)]₂ precipitated in neat THF, interfering with the spectrophotometric monitoring, and (ii) the kinetics were too rapid to follow in neat CH₃CN.

Table 1. Crystallographic Data

	<i>RRSS</i> -[Ni(tmc)](OTf)·NaOTf	<i>RRSS</i> -[Ni(tmc)SC ₆ H ₅](OTf)	<i>RSRS</i> -[Ni(tmc)SC ₆ H ₅](PF ₆)
formula	C ₁₆ H ₃₂ F ₆ N ₄ NaNiO ₆ S ₂	C ₂₁ H ₃₇ F ₃ N ₄ NiO ₃ S ₂	C ₂₀ H ₃₇ F ₆ N ₄ NiPS
fw	636.3	573.4	569.3
color, habit	blue-green plate	red-orange block	dark orange block
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> , Å	24.690(13)	12.648(3)	13.037(5)
<i>b</i> , Å	11.261(5)	15.145(4)	15.407(7)
<i>c</i> , Å	9.681(6)	14.765(4)	13.706(7)
β, deg	91.03(4)	113.96(2)	113.53(3)
<i>V</i> , Å ³	2691(2)	2584(1)	2524(2)
<i>Z</i>	4	4	4
<i>T</i> , K	296	240	246
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
ρ(calcd), g cm ⁻³	1.570	1.474	1.498
μ, cm ⁻¹	9.22	9.64	9.75
<i>R</i> (<i>F</i>), <i>R</i> _w (<i>F</i>) ^a	0.050, 0.059	0.059, 0.087	0.064, 0.073

$$^a R(F) = \sum \Delta / \sum (F_o); R_w(F) = \sum [\Delta w^{1/2}] / [\sum F_o w^{1/2}]; \Delta = |F_o - F_c|; w^{-1} = \sigma^2(F_o) + gF_o^2.$$

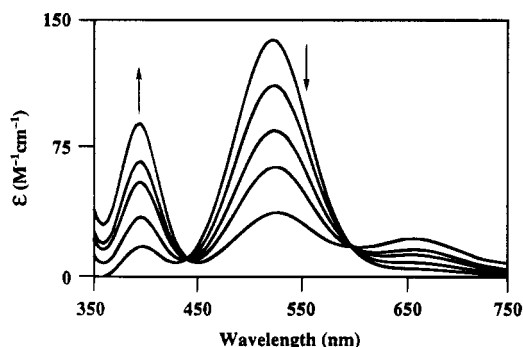


Figure 1. UV–visible spectral titration (acetone) of *RSRS*-[Ni(tmc)]-(OTf)₂ (5.0 mM) with (CH₃)₂S (0, 2.8, 5.5, 6.9, and 9.3 M, respectively) at 25 °C.

Table 2. Equilibrium Binding Constants for *RSRS*-[Ni(tmc)](OTf)₂ Measured in Acetone at 25 °C

L	<i>K</i> , M ⁻¹	L	<i>K</i> , M ⁻¹
(CH ₃) ₂ S	0.10	SC ₆ H ₅ ⁻	>10 ⁶ ^b
CH ₃ SC ₂ H ₅	0.08	(CH ₃) ₂ SO	1.0 ^a
CH ₃ SC ₆ H ₅	0	H ₂ O	0.50 ^a
(C ₆ H ₅) ₂ S ₂	0	CH ₃ CN	3.0 ^a

^a Reference 12. ^b Measured in CH₃CN.

in acetone to yield high spin, five-coordinate species. Binding is accompanied by distinct electronic spectral changes. For example, addition of (CH₃)₂S to *RSRS*-[Ni(tmc)](OTf)₂ resulted in disappearance of the 523 nm band with concomitant appearance of a band at 395 nm, Figure 1. Isosbestic points occurred at 440 and 600 nm. Binding constants were extracted from spectral titrations, Table 2. These spectroscopic changes are consistent with those reported for [Ni(tmc)](OTf)₂ in donor solvents such as H₂O, Me₂SO, and CH₃CN.¹² Under these conditions, *RSRS*-[Ni(tmc)](OTf)₂ forms five-coordinate, square pyramidal complexes while *RRSS*-[Ni(tmc)](OTf)₂ binds two solvent molecules in axial positions yielding six-coordinate derivatives. Dialkylsulfides bind weakly to [Ni(tmc)](OTf)₂. Even with [(CH₃)₂S] of 9 M, *RRSS*-[Ni(tmc)](OTf)₂ formed the five-coordinate adduct. Binding constants were relatively insensitive (± 10%) to the Ni isomer. Aryl-substituted sulfides, as exemplified by thioanisole, showed no evidence of binding even at 5 M concentrations.

The disulfides (C₂H₅)₂S₂ and (C₆H₅)₂S₂ showed no evidence of coordinating to either isomer of [Ni(tmc)](OTf)₂. The thiolates SC₆H₅⁻ and SC₂H₅⁻ bind strongly to [Ni(tmc)](OTf)₂ yielding high spin, five-coordinate species in acetonitrile. The equilibrium constant for SC₆H₅⁻ binding to *RSRS*-[Ni(tmc)]-

(OTf)₂, as measured spectrophotometrically and electrochemically in acetonitrile, is ca. 10⁶ M⁻¹.

MeCoM Binding to *RSRS*-[Ni(tmc)](OTf)₂. In contrast to organic sulfides, MeCoM binds avidly to *RSRS*-[Ni(tmc)](OTf)₂. Stoichiometric amounts of MeCoM are sufficient to observe complete binding (*K*^{MeCoM} > 10⁶ M⁻¹). ¹H NMR and IR spectra are consistent with MeCoM binding to Ni through the SO₃⁻. In the ¹H NMR spectrum (acetone-*d*₆), the methylene protons of MeCoM resonate at -5.4 ppm (CH₂SO₃⁻) and -0.6 ppm (CH₂CH₂SO₃⁻) while the methyl protons occur furthest downfield -0.04 ppm (CH₃S). In the IR spectrum, the ν_{SO} bands are shifted from 1195 cm⁻¹ for uncomplexed MeCoM to 1245 cm⁻¹, with a reduction in intensity of more than 50% accompanying binding to *RSRS*-[Ni(tmc)](OTf)₂. Binding through the sulfonate is expected based on favorable electrostatic attraction between the 2+ charged Ni ion in *RSRS*-[Ni(tmc)](OTf)₂ and the negatively charged SO₃⁻. Other anionic ligands, such as N₃⁻,^{14a} OH⁻, and SR⁻, exhibit similar high affinities for *RSRS*-[Ni(tmc)](OTf)₂. *In vivo*, the sulfonate is most likely involved in H-bonding to residues near the active site of F₄₃₀ which deactivates this group towards binding at Ni and probably directs the thioether of the substrate toward the Ni ion.^{2,6b} Additionally, the hydrocorphinoid macrocycle in F₄₃₀ carries a single anionic charge which renders the Ni(I) complex electro-neutral and less likely to bind MeCoM through the sulfonate. The former may be significant in understanding the inability of F₄₃₀ to liberate CH₄ from MeCoM *in vitro*. Under these conditions the sulfonate may compete effectively with the thioether for ligation at Ni. By binding to the Ni ion, the sulfonate occupies an open coordination site which is needed for catalysis. Results presented above suggest that for *RSRS*-[Ni(tmc)](OTf)₂, *K*^{SO₃⁻} ≥ 10⁷ K^{R₂S}.

Synthesis of [Ni(tmc)](OTf). The cyclic voltammogram of *RSRS*-[Ni(tmc)](OTf)₂ in CH₃CN exhibited a single, electrochemically reversible (Δ*E* = 65 mV) redox couple at -780 mV (vs Ag/AgCl). The *RRSS* isomer is somewhat more difficult to reduce in CH₃CN: *E*_{1/2} = -960 mV. In acetone, both isomers are reduced at identical potentials, *E*_{1/2} = -780 mV. The different redox potentials in CH₃CN reflect different affinities of the Ni(II) derivatives for CH₃CN. Chemical reduction was accomplished by stirring THF–CH₃CN (10:1) solutions of [Ni(tmc)](OTf)₂ over 0.3% Na/Hg for 30 min. Filtration through Celite yielded a blue solution from which [Ni(tmc)](OTf) was precipitated in greater than 90% yield by addition of Et₂O and hexanes. UV–visible spectroscopic data were consistent with values reported in the literature,^{11b,c} while

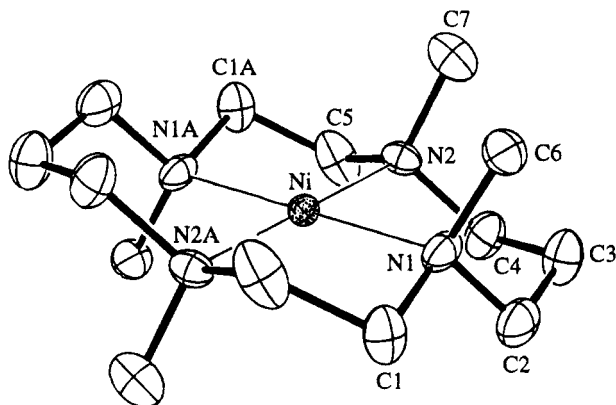


Figure 2. ORTEP of $RRSS-[Ni(tmc)](OTf) \cdot Na(OTf)$ displaying the $Ni(tmc)$ cation only. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

analytical data agreed with the formula $[Ni(tmc)](OTf) \cdot NaOTf$. This stoichiometry was confirmed by a single-crystal X-ray diffraction study. In the solid state and in the absence of O_2 , $[Ni(tmc)](OTf)$ is stable for several months.

The isomeric integrity of the Ni derivatives is not maintained upon reduction. Chemical reduction of either Ni(II) isomer resulted in production of both the *RSRS* and *RRSS*-Ni(I) isomers. Isomerization following chemical reduction of $Ni(tmc)^{2+}$ was first discussed by Espenson.^{11a} Upon initial reduction, the product ratio, measured by cyclic voltammetry in CH_3CN , favored the starting Ni(II) isomer by 80%:20%.

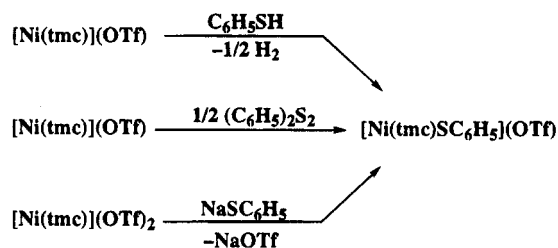
Organic Sulfide Binding to $[Ni(tmc)](OTf)$. $[Ni(tmc)](OTf)$ showed no evidence of reacting with thioethers including MeCoM nor thiolates in organic solvents. Our results are consistent with the strong preference of Ni(I) for square planar coordination. This has been confirmed by structural determination of $[Ni(tmc)](OTf)$. However, Meyerstein has reported methane production (10%) from MeCoM and similar Ni(I) macrocycles, $Ni(Me_{10}[14]aneN_4)^+$ and $Ni(tc2)^+$, in aqueous media.^{6b}

Molecular Structure of $RRSS-[Ni(tmc)](OTf) \cdot Na(OTf)$. Crystals of $RRSS-[Ni(tmc)](OTf)$ suitable for X-ray analysis were grown by vapor diffusion of Et_2O into saturated THF solutions. Despite the presence of both the *RSRS* and *RRSS* isomers in solution, the latter crystallized selectively presumably due to its lower solubility in $THF-Et_2O$. $RRSS-[Ni(tmc)](OTf)$ cocrystallized with one equivalent of $Na(OTf)$. The crystal structure consists of discrete ions with no close contacts between the $Ni(tmc)^+$ and OTf^- . A view of the cation is shown in Figure 2. Selected bond lengths and angles are contained in Table 3. The Ni ion is located on a crystallographic inversion center which relates opposite halves of the macrocycle. The coordination environment is rigorously planar (sum of the $\angle N-Ni-N$ equals 360.0°) with two distinct Ni-N distances, 2.120(5) and 2.095(5) Å. The ligand resides in the *RRSS* configuration with unexceptional metric parameters. Two experimentally different Ni-N bond distances in square planar Ni(I) and Ni(II) complexes is becoming an increasingly common phenomena.¹⁸ In fact, EXAFS experiments on $Ni(I)-F_{430M}$ revealed two distinct Ni-N distances of 1.88(3) and 2.03(3) Å.¹⁹ In the present case, the average Ni-N distance increased by 0.12 Å upon reduction from $[Ni(tmc)]^{2+}$ to $[Ni(tmc)]^+$ to accommodate

Table 3. Selected Bond Distances (Å) and Angles (deg)

<i>RRSS</i> - $[Ni(tmc)](OTf) \cdot Na(OTf)$			
Ni-N(1)	2.120(5)	Ni-N(1A)	2.120(5)
Ni-N(2)	2.095(5)	Ni-N(2A)	2.095(5)
N(1)-Ni-N(2)	93.8(2)	N(1)-Ni-N(2A)	86.2(2)
N(1)-Ni-N(1A)	180.0(1)	N(2)-Ni-N(2A)	180.0(1)
N(2)-Ni-N(1A)	86.2(2)	N(1A)-Ni-N(2A)	93.8(2)
<i>RRSS</i> - $Ni(tmc)SC_6H_5](OTf)$			
Ni-S(1)	2.369(2)	Ni-N(3)	2.080(6)
Ni-N(1)	2.157(6)	Ni-N(4)	2.115(8)
Ni-N(2)	2.162(8)	S(1)-C(20)	1.755(8)
Ni-S(1)-C(20)	120.3(2)	N(1)-Ni-N(3)	159.5(2)
S(1)-Ni-N(1)	93.6(1)	N(1)-Ni-N(4)	84.0(3)
S(1)-Ni-N(2)	100.7(2)	N(2)-Ni-N(3)	85.0(3)
S(1)-Ni-N(3)	106.9(2)	N(2)-Ni-N(4)	160.8(2)
S(1)-Ni-N(4)	98.4(2)	N(3)-Ni-N(4)	91.1(3)
N(1)-Ni-N(2)	93.1(3)		
<i>RSRS</i> - $[Ni(tmc)SC_6H_5](PF_6)$			
Ni-S(1)	2.347(2)	Ni-N(3)	2.159(7)
Ni-N(1)	2.168(7)	Ni-N(4)	2.141(5)
Ni-N(2)	2.129(6)	S(1)-C(26)	1.769(6)
Ni-S(1)-C(26)	115.2(2)	N(1)-Ni-N(3)	162.9(2)
S(1)-Ni-N(1)	99.8(2)	N(1)-Ni-N(4)	91.3(2)
S(1)-Ni-N(2)	113.2(2)	N(2)-Ni-N(3)	92.3(2)
S(1)-Ni-N(3)	97.1(1)	N(2)-Ni-N(4)	147.8(2)
S(1)-Ni-N(4)	99.0(1)	N(3)-Ni-N(4)	83.3(2)
N(1)-Ni-N(2)	83.7(3)		

Scheme 1



the larger Ni(I) ion. Similar macrocycle core expansions of 0.11 Å for *C-R,S,S,R*- $Ni(htim)^{2+/+}$ and 0.13 Å for $Ni(diene)^{2+/+}$ have been observed.^{18,20} However, for more constrained ligands, $Ni(tc1)^{2+/+}$ and $Ni(tc2)^{2+/+}$, the core size remained unchanged upon reduction.²¹ Clearly, the *tmc* ligand is sufficiently flexible to accommodate a range of metal ion sizes or specifically, in the present case, Ni(II) and Ni(I) ions.

Synthesis of $[Ni(tmc)SC_6H_5](OTf)$. Five-coordinate $[Ni(tmc)SC_6H_5](OTf)$, may be prepared by a variety of routes, Scheme 1. Oxidative addition of C_6H_5SH or $(C_6H_5)_2S_2$ to $[Ni(tmc)](OTf)$ yielded $[Ni(tmc)SC_6H_5](OTf)$. In the former, the thiol protons were liberated as H_2 . The disulfide reaction is discussed in detail below. Each of these reactions resulted in mixtures of *RSRS*- and *RRSS*- $[Ni(tmc)SC_6H_5](OTf)$ as a consequence of equilibration between the isomers in the starting Ni(I) species. Consequently, procedures commencing with Ni(II) precursors are desirable to ensure isomeric integrity of the Ni product. In a typical reaction, one equivalent of $NaSC_6H_5$ was added to $[Ni(tmc)](OTf)_2$ in THF under an Ar atmosphere. An immediate change from a suspension of the complex to an intense orange solution accompanied the reaction. $[Ni(tmc)SC_6H_5](OTf)$ was isolated by addition of Et_2O and hexanes. In

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(19) (a) EXAFS of F_{430M} : Furenli, L. R.; Renner, M. W.; Fajer, J. *J. Am. Chem. Soc.* **1990**, *112*, 8987-8989. (b) EXAFS of F_{430} : Shiemke, A. K.; Kaplan, W. A.; Hamilton, C. L.; Shelnutt, J. A. *J. Biol. Chem.* **1989**, *264*, 7276-7284.

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(21) (a) Suh, M. P.; Shin, W.; Kim, H.; Koo, C. H. *Inorg. Chem.* **1987**, *26*, 1846-1852. (b) Suh, M. P.; Kang, S.; Goedken, V. L.; Park, S. *Inorg. Chem.* **1991**, *30*, 360-365. (c) Suh, M. P.; Kim, H. K.; Kim, M. J.; Oh, K. Y. *Inorg. Chem.* **1991**, *30*, 3620-3625.

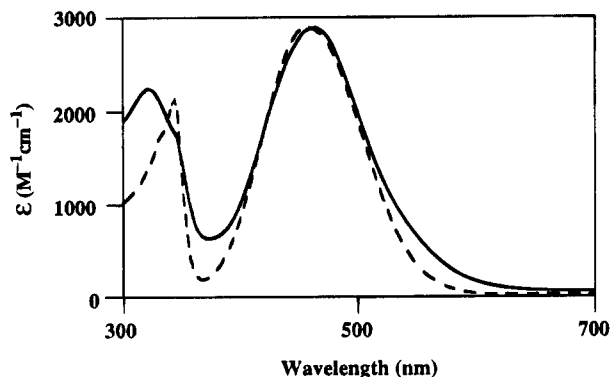


Figure 3. Electronic spectra (THF) of *RRSS*-[Ni(tmc)SC₆H₅](OTf) (---) and (b) *RSRS*-[Ni(tmc)SC₆H₅](PF₆) (—).

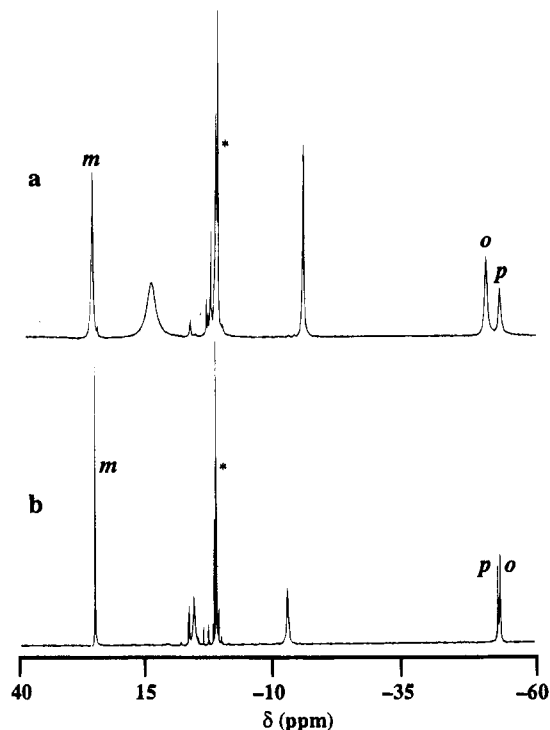


Figure 4. ¹H NMR spectra (acetone-*d*₆ = *) of (a) *RRSS*-[Ni(tmc)SC₆H₅](OTf) and (b) *RSRS*-[Ni(tmc)SC₆H₅](PF₆).

the solid state [Ni(tmc)SC₆H₅](OTf) is stable to O₂ and moisture for several hours. In solution, [Ni(tmc)SC₆H₅](OTf) exhibits diminished stability to these antagonists. The electronic spectrum of each isomer is dominated by a ligand-to-metal charge transfer band at approximately 470 nm (Figure 3). The complexes exhibit diagnostic ¹H NMR spectra which show contact shifts consistent with their high spin state (*S* = 1), Figure 4. The aryl proton resonances are well removed from the diamagnetic region of the spectrum. The *ortho* and *para* protons resonate at high field, -50 ppm, while the *meta* protons are considerably deshielded, 20 ppm. The signs of the contact shifts are consistent with π spin delocalization through the aromatic substituent. For example, shifts of similar sign and magnitude are observed for the aryl ligand protons in Fe(OEP)C₆H₅ (*S* = 1/2).²² In the porphyrin complexes the *ortho* (-80 ppm) and *para* (-25 ppm) protons are highly shielded while the *meta* (20 ppm) are deshielded.

Reactions of [Ni(tmc)](OTf) with R₂S₂. Addition of R₂S₂ (R = C₆H₅, C₂H₅) to [Ni(tmc)](OTf) in THF yielded [Ni(tmc)-

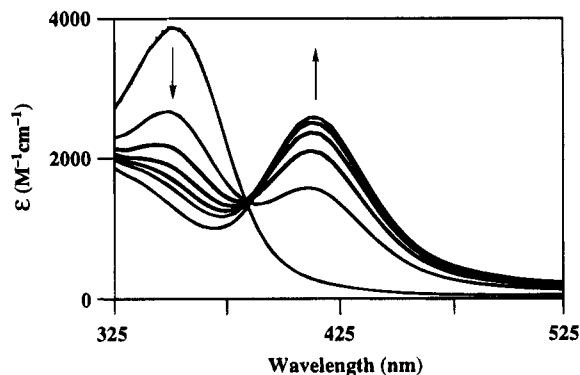
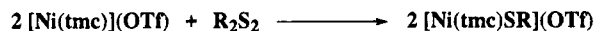
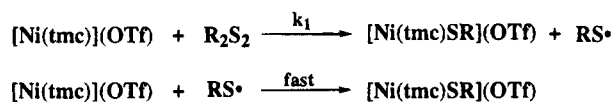


Figure 5. UV-visible spectral changes (THF) accompanying the addition of (C₂H₅)₂S₂ (0.36 M) to *RSRS*-[Ni(tmc)](OTf) (1.0 mM). Spectra were recorded every 30 min.

Table 4. Second-Order Rate Constants for Addition of R₂S₂ to [Ni(tmc)](OTf) in THF at 25 °C

R ₂ S ₂	<i>k</i> ₁ , M ⁻¹ s ⁻¹
(C ₆ H ₅) ₂ S ₂	120
(C ₂ H ₅) ₂ S ₂	1.9 × 10 ⁻³

Scheme 2



SR](OTf) as the only Ni-containing product. Electronic spectral changes accompanying the reaction (R = C₂H₅) are depicted in Figure 5. The production of [Ni(tmc)SC₂H₅](OTf) exhibited first-order kinetics over at least 3 half-lives under pseudo-first-order conditions, [(C₂H₅)₂S₂] > 10[Ni(tmc)(OTf)], as monitored by UV-visible spectroscopic changes at 414 nm. The reaction obeyed a second-order rate law: first order in each reagent. From a linear plot of *k*_{obs} vs [(C₂H₅)₂S₂], the second-order rate constant, *k*₁, was determined, Table 4. Oxidative addition of (C₆H₅)₂S₂ (*k*₁ = 120 M⁻¹ s⁻¹) to [Ni(tmc)](OTf) is notably more facile than (C₂H₅)₂S₂ (*k*₁ = 1.9 × 10⁻³ M⁻¹ s⁻¹). This significantly faster reaction could not be followed by conventional spectrophotometry. The rates were approximated by variable sweep rate cyclic voltammetry as described in the Experimental Section. The relative rates reflect differences in the S-S bond dissociation energies (C₆H₅S-SC₆H₅, 55 kcal mol⁻¹; C₂H₅S-SC₂H₅, 74 kcal mol⁻¹).²³ Products and the kinetic behavior are consistent with the mechanism contained in Scheme 2. The first step entails Ni-SR bond formation and thiyl radical production. We view this as proceeding via inner sphere electron transfer from Ni(I) to R₂S₂. In the fast second step, the thiyl radical is trapped by a second [Ni(tmc)](OTf) to yield product. Precedent for the latter reaction exists. Transition metal capture of thiyl radicals in aqueous media occurs at rates near the diffusion limit. For example, Espenson has measured rate constants for C₂H₅S[•] reacting with Cr(H₂O)₆(ClO₄)₂ (4.9 × 10⁸ M⁻¹ s⁻¹) and Ni([14]aneN₄)(ClO₄)₂ (< 3 × 10⁶ M⁻¹ s⁻¹).²⁴ Similarly, [Ni(tmc)](OTf) has been demonstrated to efficiently capture carbon-centered radicals.^{9a,11a,b}

Molecular Structures of *RSRS*-[Ni(tmc)SC₆H₅](OTf) and *RRSS*-[Ni(tmc)SC₆H₅](PF₆). The molecular structure of each isomer consists of discrete ions. A view of the cations is shown in Figure 6. Selected bond lengths and angles are contained in

(22) (a) Cocolios, P.; LaGrange, G.; Guillard, R. *J. Organomet. Chem.* **1983**, 253, 65-79. (b) Balch, A. L.; Renner, M. W. *Inorg. Chem.* **1986**, 25, 303-307.

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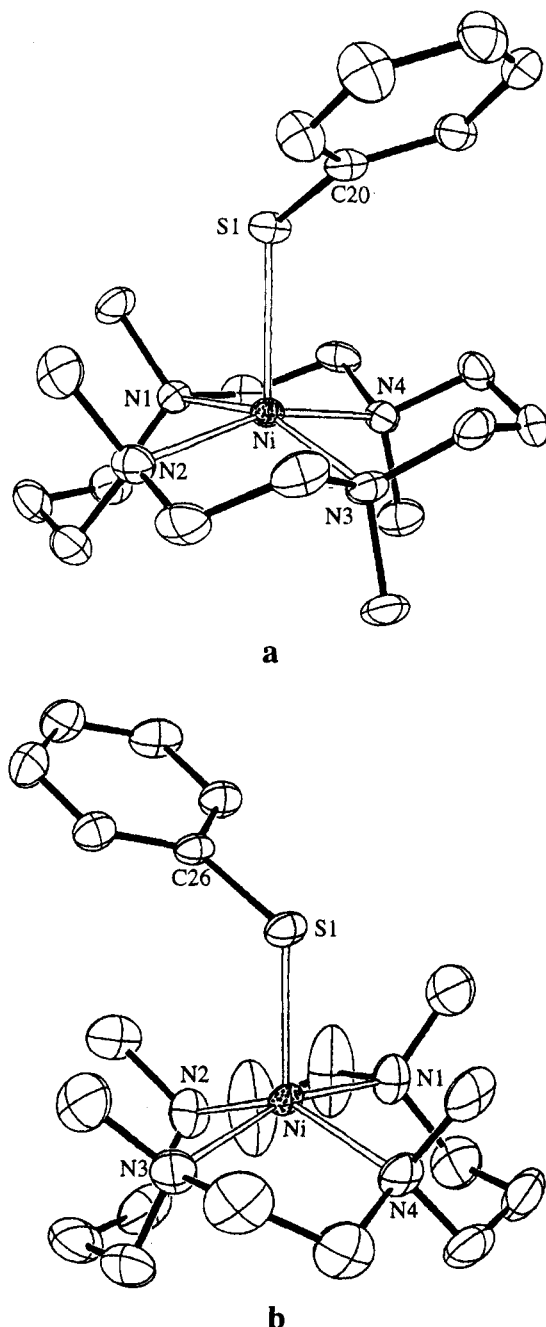


Figure 6. ORTEPs of (a) $RRSS-[Ni(tmc)SC_6H_5](OTf)$ and (b) $RSRS-[Ni(tmc)SC_6H_5](PF_6)$ displaying the cations only. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3. This study represents the first in which five-coordinate derivatives of each isomer have been structurally characterized and provides the unique opportunity to evaluate metrical differences between the two isomers. The geometry about the Ni ion in $RRSS-[Ni(tmc)SC_6H_5](OTf)$ is close to an idealized square pyramid. The four amine nitrogens provide basal ligation with Ni–N distances averaging 2.128(14) Å and the sulfur occupies the apical position, Ni–S, 2.369(2) Å. The S–Ni–N angles range from 93.6 to 106.9°. The $\angle Ni-S-C(20)$ of 120.3-(2)° is comparable to that of other metal thiolates.²⁵ The C_6H_5 substituent resides directly above N(3) as evidenced by the

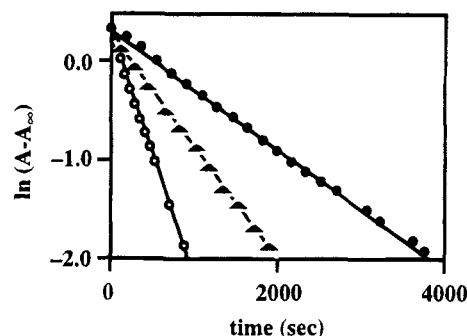
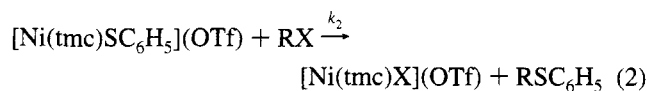


Figure 7. Pseudo-first-order plots of the alkylation of $RRSS-[Ni(tmc)SC_6H_5](OTf)$ (0.50–1.0 mM) with CH_3I (●, 7.0 mM; ▲, 13 mM; ○, 28 mM) in THF– CH_3CN (1:1) at 25 °C.

$N(3)-Ni-S-C(20)$ dihedral angle of 1.20°. Since the CH_3 group on N(3) points away from the thiolate ligand, the orientation of the aryl minimizes steric repulsions between it and the macrocycle. The gross structural features of $RSRS-[Ni(tmc)SC_6H_5](PF_6)$ are similar to $RRSS-[Ni(tmc)SC_6H_5](OTf)$. As with every other crystallographically characterized derivative,²⁶ the axial ligand is located on the same face of the tmc as the four amine CH_3 substituents. The average Ni–N distances (2.149(13) Å) of $RSRS-[Ni(tmc)SC_6H_5](PF_6)$ are longer than for the $RRSS$ isomer by 0.021 Å. These are somewhat offset by a shorter Ni–S bond, 2.352(2) Å. The $\angle Ni-S-C(26)$ is more acute by 5.1°. This is surprising because the repulsive steric interactions between the thiolate and tmc appear more demonstrative in this isomer. One of the amine nitrogens, N(2), which is nearly eclipsed by the S–C vector (dihedral angle equals 5.1°), is markedly displaced below the least-squares plane defined by the remaining N atoms, resulting in a distorted square pyramidal coordination sphere. The movement of N(2) may be rationalized as abating repulsive interactions between the C_6H_5 substituent and the CH_3 group on N(2). The closest contact is 3.36 Å (C(12)–C(26)). The average Ni–N distances are comparable with those in other structurally characterized $Ni(tmc)X^+$ complexes and are in accord with the high spin state.²⁶ For example, in $RSRS-[Ni(tmc)N_3](ClO_4)$, Ni– N_{av} equals 2.103 Å,^{26b} and in $RSRS-[Ni(tmc)(NCCH_3)](ClO_4)_2$, Ni– N_{av} equals 2.143 Å.^{26d} The differences in ground state structures of the two isomers, particularly the nickel–ligand bond distances, are manifest in the relative rates of reaction with haloalkanes.

Alkylation of $[Ni(tmc)SC_6H_5](OTf)$. Reaction of $[Ni(tmc)SC_6H_5](OTf)$ with haloalkane in THF– CH_3CN (1:1) results in quantitative formation of the products indicated in eq 2. The



rates of reaction were monitored by UV–visible spectral changes which exhibited isosbestic behavior. Under pseudo-first-order conditions, $[RX] > 20 [Ni(tmc)SC_6H_5(OTf)]$, the alkylation exhibited first-order kinetics over at least three half-lives, Figure 7. The reaction obeyed a second-order rate law: first order in each reagent, Table 5. Second-order rate constants are listed in Table 6. The trend of rate constants for RI, R =

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Table 5. Dependence of k_{obs} on [RX] for Reaction of [Ni(tmc)SC₆H₅](OTf) with RX in THF-CH₃CN (1:1) at 25 °C

RX	[RX], M	$10^3 k_{\text{obs}}$, s ⁻¹
C ₂ H ₅ I	RRSS-[Ni(tmc)SC ₆ H ₅](OTf)	
	0.0083	1.1
	0.016	1.9
	0.044	7.3
	0.12	21
	0.28	33
(CH ₃) ₂ CHI ^a	0.22	0.65
	0.45	0.84
	0.65	1.6
	1.0	1.9
	1.3	2.1
	1.9	2.4
C ₆ H ₅ CH ₂ Cl	0.014	2.1
	0.029	3.5
	0.058	7.6
	0.10	12
	0.16	21
	0.22	25
CH ₃ I	RSRS-[Ni(tmc)SC ₆ H ₅](OTf)	
	0.066	1.2
	0.17	3.0
	0.25	3.1
	0.35	5.3
	0.78	9.1
C ₂ H ₅ I	1.17	14
	0.24	0.11
	0.47	0.18
	0.87	0.43
	1.4	0.67
	1.9	0.72

^a Measured in 100% CH₃CN.**Table 6.** Second-Order Rate Constants for Alkylation of [Ni(tmc)SPh](OTf) in THF-CH₃CN (1:1) at 25 °C

RX	k_2 , M ⁻¹ s ⁻¹	
	RSRS-[Ni(tmc)SC ₆ H ₅](OTf)	RRSS-[Ni(tmc)SC ₆ H ₅](OTf)
CH ₃ I	1.2×10^{-2}	4.1
C ₂ H ₅ I	4.0×10^{-4}	0.14
(CH ₃) ₂ CHI	$\approx 7.1 \times 10^{-6}$	1.1×10^{-3}
C ₆ H ₅ CH ₂ Cl		0.12

CH₃ > C₂H₅ > (CH₃)₂CH, is consistent with S_N2 alkylation of the thiolate. Alkylation of metal thiolates may lead to isolable metal-bound thioethers.^{25,27} However, in the present case the thioether is a weaker ligand than I⁻ and does not effectively compete for the available coordination site. Significantly, the rates of alkylation of the two Ni isomers exhibit large differences. For a given RX, *ca.* $k_2^{\text{RRSS}}/k_2^{\text{RSRS}} = 350$. Taken together, the rate law, the rate dependence on RX and the rate differences between the isomers are consistent with alkylation at Ni-bound thiolate. Were alkylation to occur at unbound thiolate, mixed second-order kinetics would be expected and the rates would be independent of isomer. S_N2 alkylation of metal-bound thiolates has been demonstrated by several groups.^{25,27} A thorough kinetic study of the alkylation of CpFe(CO)₂SR yielding CpFe(CO)₂(RSR') supported a nucleophilic substitution pathway.²⁷ The effect of haloalkane (CH₃I > C₂H₅I >> (CH₃)₂CHI = (CH₃)₃CI = 0) and solvent polarity (Me₂SO > acetone) on the reaction rate were most consistent with such substitution. While the limited stability of [Ni(tmc)SC₆H₅](OTf) in a range of solvents precluded solvent polarity studies, the effect of haloalkane on reaction rates paralleled that measured for CpFe-

(CO)₂SR. The rate differences between the isomers is in accord with the relative ground state structures determined crystallographically.²⁸ RRSS-[Ni(tmc)SC₆H₅](OTf) possesses a longer Ni-S bond distance and shorter Ni-N bonds than the RSRS isomer. This is consistent with weaker Ni-SC₆H₅ bonding and consequently, a less distorted Ni coordination sphere relative to the four-coordinate complex. The (thermodynamically) weaker thiolate ligation results in a more kinetically accessible alkylation at the sulfur lone pair. Conversely, the structural variances of RSRS-[Ni(tmc)SC₆H₅](PF₆), a shorter Ni-S bond distance and more distorted macrocycle core, point to a more stable, less reactive Ni-SC₆H₅ moiety. Qualitative differences in reaction rates of the two Ni isomers have been documented previously. Reactions of haloalkanes with organonickel complexes, [Ni(tmc)R](ClO₄), showed a similar dependence on isomer identity.^{11b,c} RRSS-[Ni(tmc)R](ClO₄) reacted significantly faster than RSRS-[Ni(tmc)R](ClO₄).

In addition to a clean S_N2 pathway, deviations from second-order kinetics were observed for slower reactions ((CH₃)₂CHI and C₆H₅CH₂Cl reacting with the RSRS isomer). These data could be fit with a three term rate law which took into account Ni-SC₆H₅ bond dissociation and fast alkylation of the free SC₆H₅⁻ (see Experimental Section).²⁹

Summary

The following are the principal findings and conclusions of this study.

(1) [Ni(tmc)](OTf)₂ binds organic sulfides weakly to form high spin, five-coordinate species. (CH₃)₂S and (C₂H₅)₂S coordinate to the RSRS and RRSS isomers with equal affinities, while aryl-substituted sulfides, C₆H₅SCH₃, do not coordinate. The donor ability of the sulfides falls below that of common solvents: H₂O, Me₂SO, and CH₃CN.

(2) [Ni(tmc)](OTf)₂ binds MeCoM strongly in organic media: coordination, dictated by electrostatics, is via the sulfonate rather than the thioether.

(3) The Ni(I) complex, RRSS-[Ni(tmc)](OTf), has been crystallographically characterized. The Ni ion coordination sphere is rigorously planar with two sets of distinct Ni-N bond distances: 2.120(5) and 2.095(5) Å. The macrocycle core expansion is in accord with Ni-centered reduction.

(4) RSRS-[Ni(tmc)SC₆H₅](OTf) and RRSS-[Ni(tmc)SC₆H₅](OTf) may be synthesized by a variety of routes. However, to insure isomeric purity, the corresponding [Ni(tmc)](OTf)₂ must be employed as starting material.

(5) Consistent with structural differences in the solid state, RRSS-[Ni(tmc)SC₆H₅](OTf) reacts with haloalkanes 350 times more rapidly than RSRS-[Ni(tmc)SC₆H₅](OTf). Alkylation occurs at Ni-bound thiolate and not via a dissociative pathway involving Ni-SC₆H₅ bond cleavage.

(28) A reviewer has suggested the kinetic differences we observe here result from differences in accessibility of the sulfur to the electrophile, i.e., steric effects due to the presence of four methyl groups surrounding the sulfur in the RSRS diastereomer, whereas there are only two in the RRSS diastereomer. Clearly, this can not be the case as the RSRS isomer is more accessible on the side containing the four methyl groups. This contention is evidenced by the structures of five-coordinate derivatives of the RSRS isomer which **always** show the fifth ligand bound to the same side as the methyl groups. In other words, the ethylene and propylene linkers of tmc are more sterically demanding than the methyl groups. Furthermore, the kinetic and structural *trans* effects of alkyl groups have been well documented in organocobalt chemistry. (a) Stewart, R. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1978**, *100*, 817. (b) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197-5202.

(29) At high [I⁻] (added [Bu₄N]I), an I⁻-catalyzed pathway which becomes significant. In the presence of 30 equiv of I⁻, there are no UV-visible spectral changes observed for [Ni(tmc)SC₆H₅](OTf).

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Our results suggest that the $[\text{Ni}(\text{tmc})](\text{OTf})$ system is ideally suited to explore the role of the HS-HTP cofactor in promoting F_{430} catalysis. In this regard, we are currently exploiting the reaction of R_2S_2 with $[\text{Ni}(\text{tmc})](\text{OTf})$ in the presence of MeCoM to evaluate the ability of thiyl radicals to activate MeCoM towards C-S bond rupture.³⁰

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G3). C.G.R. thanks the NSF for a National Young Investigator Award (1994–1999). Garry Williams and Timothy Hubin are thanked for their assistance in the synthesis of $[\text{Ni}(\text{tmc})\text{SC}_6\text{H}_5](\text{OTf})$ and $[\text{Ni}(\text{tmc})](\text{OTf})$, respectively. We thank the reviewers for their helpful comments.

Supporting Information Available: Tables giving structure determination summary, atomic coordinates, complete bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom parameters for $\text{RRSS}-[\text{Ni}(\text{tmc})](\text{OTf})$, $\text{RSRS}-[\text{Ni}(\text{tmc})\text{SC}_6\text{H}_5](\text{PF}_6)$, and $\text{RRSS}-[\text{Ni}(\text{tmc})\text{SC}_6\text{H}_5](\text{OTf})$ (27 pages). Ordering information is given on any current masthead page.

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