Linkage Isomerization of MSCN(CDOH)$_2$(CDO)BMe to MNCS(CDOH)$_2$(CDO)BMe (M = Tc, Re). Crystal Structures of TcNCS(CDOH)$_2$(CDO)BMe, ReNCS(CDOH)$_2$(CDO)BMe, and ReSCN(CDOH)$_2$(CDO)BMe[†]

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The 7-coordinate technetium(III) and rhenium(III) monocapped tris(dioxime) complexes [MX(dioxime)$_3$BR] have been prepared in which the seventh ligand, X, is thiocyanate or hydroxide (M = Tc, Re; R = Me, Et). Both the N- and S-bound thiocyanate linkage isomers are produced during the syntheses, however, the S-bound complex isomerizes to the N-bound analogue. The synthetic routes employed allowed isolation of sufficient quantities of the technetium and rhenium S-bound isomers to be identified; however, full characterization was not possible. The linkage isomerization reaction of TcSCN(CDOH)$_2$(CDO)BMe to TcNCS(CDOH)$_2$(CDO)BMe was monitored in dichloromethane by UV−visible spectrophotometry, with four isosbestic points observed, consistent with the formation of a single product. The N-bound isomers for both Tc and Re, and the S-bound isomer of Re were characterized by single-crystal X-ray diffraction analysis. The two N-bound complexes were found to be isostructural. TcNCS(CDOH)$_2$(CDO)BMe crystallized in the orthorhombic space group $P2_12_12_1$ with $a = 15.814(2)$ Å, $b = 17.855(3)$ Å, $c = 17.997(5)$ Å, $Z = 8$, $R = 0.054$, and $R_W = 0.057$. ReNCS(CDOH)$_2$(CDO)BMe crystallized in the orthorhombic space group $P2_12_12_1$ with $a = 15.795(1)$ Å, $b = 17.843(2)$ Å, $c = 18.014(3)$ Å, $Z = 8$, $R = 0.054$, and $R_W = 0.073$. In both cases two independent molecules per unit cell were observed. ReSCN(CDOH)$_2$(CDO)BMe crystallized in the monoclinic space group $P2_1/c$ with $a = 10.0866(6)$ Å, $b = 26.301(2)$ Å, $c = 12.4592(7)$ Å, $\beta = 100.5(1)$ deg, $Z = 4$, $R = 0.100$, and $R_W = 0.141$.

Introduction

Treatment of tris-dioxime complexes of Fe,[1,2] Co[3−5] and Ru[6] with boronic acids yield bis-capped clathrochelate complexes of the type [M(dioxime)$_3$(BR)$_2$], where R is any of a variety of organic groups or hydroxide. Technetium(III) and rhenium(III) form seven-coordinate monocapped tris-dioxime species of formula MX(dioxime)$_3$BR, where X is a monodentate anion (generally a halide).[7−9] The seventh ligand (X) prevents the second boronic acid from capping the molecule to yield the clathrochelate structure.[7]

The boronic acid adducts of technetium dioxime complexes (better known as BATOs) were developed as myocardial and cerebral perfusion imaging agents.[10,11] The seventh ligand is susceptible to hydrolysis at pH 6 and higher, yielding hydroxide in the seventh coordination site.[12] The rates of hydrolysis of the seventh ligand are dependent on the identity of this group, with slower rates observed for smaller and harder ligands.[12] We pursued the chemistry involving the seventh ligand for both the BATOs and the rhenium analogues, the BAReOs (boronic acid adducts of rhenium dioximes), with thiocyanate. The thiocyanate ligand, because of its ambidentate nature, allowed us to probe the hypothesis that smaller and harder ligands were preferred in the seventh coordination site in these complexes.

In principle, this pseudohalide is ambidentate and able to coordinate to metals through either the sulfur or the nitrogen, with examples of both N- and S-coordination well-known.[13−21] Though one linkage isomer will generally be thermodynamically

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more stable, the less favored isomer can often be isolated if the reaction conditions are carefully tuned.[13,17,20,21] In the case of the Tc(III) BATO and Re(III) BAReO complexes, the thermodynamically more stable isomer was found to be the N-bound isothiocyanate. The S-bound thiocyanate, which was seen to form concurrent with the N-bound isothiocyanate, isomerizes to the N-bound analogue in solution. We previously reported preliminary results on these linkage isomers.[22] We report here our studies investigating thiocyanate/isothiocyanate as the seventh ligand for both BATO and BAReO complexes, including X-ray crystal structures of both linkage isomers. This is the first case, to our knowledge, that thiocyanate has coordinated through the sulfur to either Tc or Re in any oxidation state.

Experimental Section

Abbreviations. The following abbreviations are used throughout: NCS, isothiocyanate; SCN, thiocyanate; FAB-MS, fast atom bombardment mass spectrometry; HPLC, high performance liquid chromatography; FT-IR, Fourier transform infrared.

General Procedures. ***Caution!*** Standard radiation safety procedures were followed at all times when handling ^{99}Tc and ^{99m}Tc isotopes. Technetium-99m emits a 140 keV γ-ray with a half-life of 6.0 h. Technetium-99 emits a 0.292 MeV β^- particle with a half-life of 2.1 $\times 10^5$ years. Milligram quantities of ^{99}Tc can be adequately shielded using normal laboratory glassware.

Infrared spectra were obtained from KBr pellets or Nujol mulls and recorded on a Sirius 100 or a Nicolet 20DXB FT-IR spectrometer. ^{1}H NMR spectra were obtained in CD_2Cl_2 or $CDCl_3$ using a 400-MHz JEOL-GX-400, a Bruker ARX-250 or a Bruker AMX-500 spectrometer. Fast atom bombardment (FAB) mass spectra were run from a thioglycerol matrix on a VG-ZAB-2F spectrometer. Chemical ionization (CI) mass spectra were run in a glycerol matrix on a Finnigan TSQ spectrometer. UV−visible spectra were recorded on a Hewlett-Packard HP 8451A or 8452A diode-array spectrophotometer. Elemental analyses were performed by the Bristol-Myers Squibb Microanalytical Laboratory (Princeton, NJ), Desert Analytics Laboratory (Tucson, AZ), or Quantitative Technologies Inc. (Whitehouse, NJ). HPLC chromatograms were obtained, unless otherwise indicated, on a Nucleosil C_8 (15 cm, 4.6 mm i.d., 5 μ) reversed phase column plus 3 cm guard column using 70/30 CH_3CN/citric acid (0.1 M) as the mobile phase at a flow rate of 1 mL/min, using a Perkin-Elmer HPLC system (Series 410 LC quaternary pump) interfaced to PE Nelson Turbochrome 3.3 software, with UV−visible (400 nm) or NaI(Tl) detection.

Materials. 1,2-Cyclohexanedione dioxime ($CDOH_2$), methylboronic acid, and trifluoromethanesulfonic acid were obtained from Aldrich Chemical Co. Ethylboronic acid was available from a previous study.[9] Unless otherwise noted, all chemicals were of reagent grade and used as received. The $NH_4{}^{99}TcO_4$ was purchased from Oak Ridge and purified before use to remove TcO_2 (by either H_2O_2 oxidation or water dissolution followed by filtration). The $^{99m}TcO_4{}^-$ in saline was eluted from a Bristol-Myers Squibb ^{99}Mo/^{99m}Tc generator.

$ReCl(CDOH)_2(CDOH_2)$,[7] $ReCl(CDOH)_2(CDO)BR$ (R = Me, Et), and $^{99}TcCl(CDOH)_2(CDO)BMe$[9] were prepared according to literature methods. Analyses (^{1}H and ^{13}C NMR, UV−vis) were consistent with the literature values.

Isothiocyanato- and Thiocyanato[bis[(1,2-cyclohexanedione dioximato)(1−)-*O*][(1,2-cyclohexanedione dioximato)(2−)-*O*]methylborato(2−)-*N*,*N′*,*N″*,*N‴*,*N″″*,*N″‴*]technetium(III), $^{99}TcNCS(CDOH)_2(CDO)BMe$ and $^{99}TcSCN(CDOH)_2(CDO)BMe$. This reaction was carried out in a dark hood because the thiocyanate isomer slowly isomerizes to the isothiocyanate analogue. $CDOH_2$ (0.312 g, 2.20 mmol) and $(HO)_2BMe$ (0.056 g, 0.93 mmol) were dissolved in 10 mL of ethanol. To this stirred solution was added a 20 mL aqueous solution containing $NH_4{}^{99}TcO_4$ (0.112 g, 0.619 mmol) and NaNCS (0.140 g, 1.73 mmol). The pH of the reaction mixture was adjusted to 2−3 with dilute aqueous trifluoromethanesulfonic acid (ca. 1 M). Stannous tartrate (0.332 g, 1.24 mmol) suspended in ca. 1 mL of dilute trifluoromethanesulfonic acid was added dropwise over 2 min upon which the reaction mixture became an intense orange brown in color. The reaction was then heated at reflux for ca. 45 min, cooled, and exhaustively extracted with CH_2Cl_2 (until no more orange brown color was observed in the organic fraction). The combined CH_2Cl_2 extracts were dried through anhydrous sodium sulfate and chromatographed in the dark on a silica gel column (1 cm × 20 cm). Elution with CH_2Cl_2 displaced first the reddish $TcNCS(CDOH)_2(CDO)BMe$, which was followed closely by the brownish $TcSCN(CDOH)_2(CDO)BMe$. The tail of the first band and the front of the second overlapped somewhat. The two bands were collected in several fractions and analyzed by HPLC for purity. An equal volume of hexane was then added and the products allowed to crystallize, the N-bound isomer at room temperature by slow evaporation and the S-bound isomer in the dark and cold (freezer). Red cubic shaped crystals of $TcNCS(CDOH)_2(CDO)BMe$ resulted from the first fraction. These were collected by filtration, washed with hexane, and vacuum dried. Yield: 0.020 g (5.7%). Anal. Calcd (found) for $TcC_{20}H_{29}N_7O_6BS\cdot{}^1/_3CH_2Cl_2$: C, 38.52 (38.63); H, 4.68 (4.68); N, 15.47 (15.41). FAB mass spectra: $M^{\bullet+}/(M - H)^-$ 605/604; $M^{\bullet+}$ − NCS 547. UV−visible spectrum (CH_3CN): 476 nm (3180), 388 nm (9500), 324 nm (10 920), 232 nm (16 900). HPLC: 4.32 min. FT-IR (Nujol mull): 2052 cm^{-1} (sh; ν_{CN}). ^{1}H NMR ($CDCl_3$): 0.223 ppm (s, 3H, BCH_3); 1.7−1.9 ppm (m, 12H, $-CH_2-$); 2.8−3.2 ppm (m, 12H, $N{=}CHCH_2-$); 14.89 ppm (s, 2H, $O-H\cdots O$). ^{13}C NMR ($CDCl_3$): 20.68, 20.97, 21.52, 21.55 ppm ($-CH_2-$); 25.69, 25.85, 26.09, 26.65 ppm ($N{=}CHCH_2$); 148.25, 154.99, 157.91, 158.39 ppm ($N{=}C$).

From the latter brownish fractions, brown needles of $TcSCN(CDOH)_2(CDO)BMe$ formed, which were collected by filtration, washed with hexane, and vacuum-dried. Yield: 0.010 g (2.3%). FAB mass spectra: $(M + H)^+/(M - H)^-$ 606/604; $(M - NCS)^+$ 547. UV−visible spectrum (CH_3CN): 462 nm (3080), 380 nm (8460), 326 nm (8850), 236 nm (not determined). HPLC: 3.97 min. FT-IR (Nujol mull): 2114 cm^{-1} (sh; ν_{CN}).

Synthesis of $^{99m}Tc(NCS/SCN)(CDOH)_2(CDO)BMe$. This mixture of isomers was prepared by ligand exchange on $^{99m}TcOH(CDOH)_2(CDO)BMe$. $^{99m}TcCl(CDOH)_2(CDO)BMe$ and $^{99m}TcOH(CDOH)_2(CDO)BMe$ were prepared as previously described.[12] Briefly, $^{99m}TcCl(CDOH)_2(CDO)BMe$ was prepared by reconstituting lyophilized kits which contained $CDOH_2$, $MeB(OH)_2$, and stannous chloride as the reductant. A 1 mL amount of $^{99m}TcO_4{}^-$ generator eluent was added to the kit, and the resulting solution was then heated at 100 °C for 15 min and cooled. The desired product was separated from the nonradioactive kit components by adsorption on a plug of reversed phase PRP-1 resin. After washing the resin with 25% v/v ethanol/water, the product was eluted with absolute ethanol and the identity was verified by HPLC. $^{99m}TcOH(CDOH)_2(CDO)BMe$ was prepared by removing the ethanol from the purified $^{99m}TcCl(CDOH)_2(CDO)BMe$ under a stream of nitrogen, redissolving the residue in chloride-free phosphate buffer at pH 8.0, and heating at 37 °C for 30 min. The $^{99m}TcOH(CDOH)_2(CDO)BMe$ was isolated by the same procedure described above for $^{99m}TcCl(CDOH)_2(CDO)BMe$. Again, the ethanol was removed under a stream of nitrogen and the residue was taken up in 0.01 M trifluoromethanesulfonic acid. A 50−100 mg amount of NaNCS was added, and the reaction mixture was heated at 37 °C for 30 min. $^{99m}Tc(NCS/SCN)(CDOH)_2(CDO)BMe$ was isolated by the same procedure described above for $^{99m}TcCl(CDOH)_2(CDO)BMe$. Both

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isomers were formed as determined by HPLC. The radiochemical purity (RCP) of ^{99m}Tc(NCS/SCN)(CDOH)$_2$(CDO)BMe was greater than 95% after purification. The retention times observed for these ^{99m}Tc complexes were the same as those observed for their ^{99}Tc analogues, with about 68% of the NCS isomer formed and 32% of the SCN isomer formed.

Hydroxy[bis[(1,2-cyclohexanedione dioximato)(1−)-*O*][(1,2-cyclohexanedione dioximato)(2−)-*O*]methylborato(2−)-*N*,*N*′,*N*′′,*N*′′′,-*N*′′′′,*N*′′′′′]rhenium(III), ReOH(CDOH)$_2$(CDO)BMe. ReCl(CDOH)$_2$(CDO)BMe (0.0377 g, 0.0563 mmol) was dissolved in 17.0 mL of acetonitrile and 11.0 mL of water. The pH was adjusted to ca. 7−8 with 0.1 M NaOH. The reaction mixture was refluxed for 24 h with periodic adjustment to maintain the pH at 7−8, to facilitate the Cl−OH exchange reaction. The reaction was monitored by HPLC to ensure completion (t_R(Cl) = 3.72 min, t_R(OH) = 3.03 min). The reaction mixture was rotary evaporated to dryness and redissolved in CH_3CN. After adsorption on a silica gel column, elution with CH_2Cl_2 displaced the remaining ReCl(CDOH)$_2$(CDO)BMe as an orange band. Elution with CH_3CN and finally 80/20 CH_3CN/H_2O displaced the orange product, ReOH(CDOH)$_2$(CDO)BMe. The fractions containing the product were combined, rotary evaporated to dryness, redissolved in CH_3CN, and filtered. An equal volume of H_2O was added and the product crystallized by slow evaporation of solvent at room temperature. The orange crystalline product was collected, washed with H_2O and dried in vacuo over P_2O_5. Yield: 0.0195 g (51.4%). Elemental anal. Calcd (found) for $ReC_{20}H_{32}N_6O_7B \cdot H_2O$: C, 34.08 (33.89); H, 4.82 (4.89); N, 12.55 (12.34). UV−visible spectrum (CH_3CN): 478 nm (8490), 392 nm (11 900), 328 nm (6870). HPLC: 3.03 min. FT-IR (Nujol mull): 3584 (sh), 3551 (sh), 3320 (br) cm^{-1} (ν_{OH}). ^{1}H NMR ($CDCl_3$): 0.155 ppm (s, 3H, BC*H*$_3$); 1.6−1.85 ppm (m, 15H, −C*H*$_2$−, Re−O*H*·*H*$_2$O); 2.95−3.35 ppm (m, 12H, N=CHC*H*$_2$−); 15.35 ppm (s, 2H, O−*H*···O). ^{13}C NMR ($CDCl_3$): 20.95, 21.30, 21.76, 21.91 ppm (−*C*H$_2$−); 25.08, 25.43, 25.58, 25.72 ppm (N=CH*C*H$_2$); 146.86, 152.06, 156.06, 156.66 ppm (N=*C*).

Deuterated ReOD(CDOH)$_2$(CDO)BMe was prepared to aid in the spectral characterization of ReOH(CDOH)$_2$(CDO)BMe. This compound was prepared from ReCl(CDOH)$_2$(CDO)BMe as described above for ReOH(CDOH)$_2$(CDO)BMe substituting D_2O for H_2O in all steps of the synthesis. FT-IR (Nujol mull): 2644 (sh), 2538 (sh), 2457 (br) cm^{-1} (ν_{OD}). ^{2}H NMR (dry CH_2Cl_2): 1.85 ppm (s, 3D, Re−O*D*·*D*$_2$O); 15.21 ppm (s, 2D, O−*D*···O).

Isothiocyanato[bis[(1,2-cyclohexanedione dioximato)(1−)-*O*][(1,2-cyclohexanedione dioximato)(2−)-*O*]methylborato(2−)-*N*,*N*′,*N*′′,*N*′′′,-*N*′′′′,*N*′′′′′]rhenium(III), ReNCS(CDOH)$_2$(CDO)BMe and Thiocyanato[bis[(1,2-cyclohexanedione dioximato)(1−)-*O*][(1,2-cyclohexanedione dioximato)(2−)-*O*]methylborato(2−)-*N*,*N*′,*N*′′,*N*′′′,*N*′′′′,*N*′′′′′]-rhenium(III), ReSCN(CDOH)$_2$(CDO)BMe. These compounds were prepared simultaneously by ligand exchange on ReOH(CDOH)$_2$(CDO)BMe. ReOH(CDOH)$_2$(CDO)BMe·H_2O (0.5239 g, 0.783 mmol) was dissolved in ca. 100 mL of CH_3CN, followed by the addition of 40 mL of water and sufficient ~1 M aqueous trifluoromethanesulfonic acid to bring the pH to 2−3. An excess of NaNCS (2 g) was added, and the reaction mixture was stirred overnight in the dark until the OH complex had been converted to the products, as determined by TLC (R_f(*N*CS) ≈ 0.5, R_f(*S*CN) ≈ 0.25, silica gel, CH_2Cl_2). The crude red ReNCS(CDOH)$_2$(CDO)BMe which had precipitated from solution was collected by filtration. Water (100 mL) was added to the filtrate remaining, and it was then exhaustively extracted with CH_2Cl_2, and the CH_2Cl_2 extract was dried through anhydrous Na_2SO_4. Both the red precipitate and the filtrate extract were purified by silica gel chromatography (1 cm × 40 cm) with CH_2Cl_2 as the eluent. This separation was carried out in the dark to minimize isomerization of the S-bound to the N-bound complex. ReNCS(CDOH)$_2$(CDO)BMe, which eluted first as a red band, was dried by filtration through anhydrous Na_2SO_4. An equal volume of hexane was added and the product crystallized by slow evaporation. X-ray quality red crystals were isolated by slow diffusion of hexane into a CH_2Cl_2 solution of the product on storage at ~5 °C. 0.3229 g (59.6%) of recrystallized product was isolated by filtration, washed with hexane and air-dried. Elemental anal. Calcd (found) for $ReC_{20}H_{29}N_7O_6BS$: C, 34.68 (35.23); H, 4.19 (4.13); N, 14.16 (13.83); S, 4.62 (4.42). UV−visible spectrum ($CHCl_3$): 486 nm (7520), 406 nm (17,000), 326 nm (11,000). HPLC: 4.59 min. FT-IR (Nujol mull): 2055 (sh), 2079 (sh) cm^{-1} (ν_{CN}). ^{1}H NMR ($CDCl_3$): 0.19 ppm (s, 3H, BC*H*$_3$); 1.70−1.80 ppm (m, 12H, −C*H*$_2$−); 3.02−3.42 ppm (m, 12H, N=CHC*H*$_2$−); 15.41 ppm (s, 2H, O−*H*···O). ^{13}C NMR ($CDCl_3$): 20.82, 21.14, 21.60, 21.79 ppm (−*C*H$_2$−); 25.08, 25.72, 25.91 ppm (N=CH*C*H$_2$); 148.84, 155.41, 159.08, 160.84 ppm (N=*C*).

The yellow-brown ReSCN(CDOH)$_2$(CDO)BMe, which was the second band to elute, was collected and filtered through anhydrous Na_2SO_4 to remove any water. The sample was protected at all times from light. An equal volume of hexane was added and the product slowly crystallized in the freezer (−20 °C) to yield 0.007 g (1.3%) of brown crystals which were found suitable for X-ray diffraction analysis. UV−visible spectrum ($CHCl_3$): 466 nm, 396 nm, 328 nm (insufficient quantities available for accurate ϵ determinations). HPLC: 4.16 min. FT-IR (Nujol mull): 2118 cm^{-1} (sh, ν_{CN}). ^{1}H NMR ($CDCl_3$): 0.19 ppm (s, 3H, BC*H*$_3$); 1.60−1.94 ppm (m, 12H, −C*H*$_2$-); 3.02−3.48 ppm (m, 12H, N=CHC*H*$_2$−); 15.13 ppm (s, 2H, O−*H*···O).

Isothiocyanato[bis[(1,2-cyclohexanedione dioximato)(1−)-*O*][(1,2-cyclohexanedione dioximato)(2−)-*O*]ethylborato(2-)-*N*,*N*′,*N*′′,*N*′′′,-*N*′′′′,*N*′′′′′]rhenium(III), ReNCS(CDOH)$_2$(CDO)BEt. This compound was prepared following the procedure described above for ReNCS(CDOH)$_2$(CDO)BMe, using ReCl(CDOH)$_2$(CDO)BEt as the starting compound. IR: ν_{CN} = 2049 cm^{-1}. FAB-MS: $M^{\bullet -}/(M + H)^+ = 706/707$, $(M^{\bullet} - NCS)^- = 648$, $(M^{\bullet} - OH)^+ = 690$.

NCS/SCN−OH Exchange Reaction. The kinetics of conversion of ^{99m}Tc(NCS/SCN)(CDOH)$_2$(CDO)BMe to ^{99m}TcOH(CDOH)$_2$(CDO)BMe were determined by the method previously described.[12] Briefly, a 1 mL aliquot of phosphate buffer (pH 8.0) was placed into a 16 × 125 mm siliconized Vacutainer tube and incubated at 37 °C in a water bath. An aliquot (25−50 μL, approximately 200 μCi) of the isolated ^{99m}Tc(NCS/SCN)(CDOH)$_2$(CDO)BMe in ethanol was added, the resultant solution was mixed by shaking, and the percent activity as ^{99m}Tc(NCS/SCN)(CDOH)$_2$(CDO)BMe over time was determined by HPLC analysis using a Nucleosil C_8 (15 cm plus guard) reversed phase column with a mobile phase of 70/30 CH_3CN/0.1 M citric acid (pH 2.4), 1.5 mL/min flow rate, NaI(Tl) γ detection. No attempt was made to separate the N-bound and S-bound isomers, and the total N- plus S-bound complex was used in determining the half-life of the conversion to ^{99m}TcOH(CDOH)$_2$(CDO)BMe. The exchange rate was determined in triplicate, and linear regression analysis of ln[fraction of ^{99m}Tc(NCS/SCN)(CDOH)$_2$(CDO)BMe] versus time (in minutes) gave the pseudo-first-order rate constant and half-life of NCS/SCN → OH conversion.

S → N Linkage Isomerization Studies of ^{99}Tc(SCN)(CDOH)$_2$(CDO)BMe. The linkage isomerization reaction of ^{99}TcSCN(CDOH)$_2$(CDO)BMe to ^{99}TcNCS(CDOH)$_2$(CDO)BMe was monitored spectrophotometrically, at ambient temperature, scanning repetitively every 30 min in the region of 300−600 nm. Dichloromethane was used as the solvent for this reaction to minimize or eliminate competition by the hydrolysis reaction. HPLC analysis of the sample used for the spectophotometric study was done initially and at the end of the study using a Nucleosil C_8 (15 cm plus guard) reversed phase column with a mobile phase of 70/30 CH_3CN/0.1 M ammonium acetate (pH 4.6), 1.5 mL/min flow rate, 400 nm detection.

X-ray Crystal Structure Analyses. [TcNCS(CDOH)$_2$(CDO)BMe] and [ReNCS(CDOH)$_2$(CDO)BMe]. Deep red crystals of both [TcNCS(CDOH)$_2$(CDO)BMe] and [ReNCS(CDOH)$_2$(CDO)BMe] were obtained as described above. Intensity data were obtained on an Enraf-Nonius CAD 4 automatic diffractometer, using the $\omega - 2\theta$ scan mode with Cu Kα radiation from a graphite monochromator (λ = 1.540 56 Å). Intensities were corrected for Lorentz and polarization effects. Equivalent reflections were merged, and semiempirical absorption corrections were made using the Ψ scan technique. Space group, lattice parameters, and other relevant information for these structures are given in Table 1. Structures were solved by direct methods with full-matrix least-squares refinement, employing the NRCVAX package.[23−28] All non-hydrogen atoms were refined with anisotropic thermal parameters. The

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Table 1. Crystal Data, Data Collection Parameters, and Refinement Parameters[a]

	$TcNCS(CDOH)_2(CDO)BMe$	$ReNCS(CDOH)_2(CDO)BMe$	$ReSCN(CDOH)_2(CDO)BMe$
empirical formula	$TcC_{20}H_{29}N_7O_6SB$	$ReC_{20}H_{29}N_7O_6SB$	$ReC_{20}H_{29}N_7O_6SB \cdot CH_2Cl_2 \cdot 2H_2O$
fw	604.37	692.58	813.54
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
a, Å	15.814(2)	15.795(1)	10.0866(6)
b, Å	17.855(3)	17.843(2)	26.301(2)
c, Å	17.997(5)	18.014(3)	12.4592(7)
β, deg			100.464(1)
V, Å^3	5082(2)	5077(1)	3250(1)
Z	8	8	4
ρ_{calc}, g/cm^3	1.580	1.812	1.663
T, °C	23	23	23
μ, cm^{-1}	58.1	51.0	40.7
λ source, Å	1.5412	1.5412	0.710 73
$R(F)$	0.054	0.054	0.100
$R_w(F)$	0.057	0.073	0.141

[a] Least squares weights, $w = \sigma^{-2}(F_o)$, were calculated with the assumption that $\sigma^2 = \epsilon^2 + (\rho I)^2$ where ϵ is the statistical counting error and $\rho = 0.0224$ for TcNCS(CDOH)$_2$(CDO)BMe and ReNCS(CDOH)$_2$(CDO)BMe, and $\rho = 0.0387$ for ReSCN(CDOH)$_2$(CDO)BMe. The function minimized in the least-squares refinements were $\sum w(|F_o| - |F_c|)^2$. R is defined as $\sum||F_o| - |F_c||/\sum|F_o|$ while $R_W = [\sum_W (|F_o| - |F_c|)^2/\sum_W|F_o|^2]^{1/2}$.

hydrogen atoms were placed at calculated positions and included in the refinement using a riding model, with fixed isotropic U. The absolute configuration of the structure was determined by refinement of the η parameter.[29] The final difference map had no features of chemical significance in either structure.

[ReSCN(CDOH)$_2$(CDO)BMe]. Red-brown crystals of the S-bound isomer [ReSCN(CDOH)$_2$(CDO)BMe] proved very difficult to grow, in part due to isomerization to the N-bound isomer, [ReNCS(CDOH)$_2$(CDO)BMe]. Clumps of thin plates were grown from a CH_2Cl_2/hexane solution in the freezer. A specimen with approximate dimensions of 0.01 × 0.15 × 0.25 mm was selected for data collection. While this crystal was not entirely single, it was possible to collect data. The intensity data were collected on a Siemens SMART CCD system, using the omega scan mode with Mo Kα radiation from a graphite monochromator ($\lambda = 0.709\,30$ Å). Intensities were corrected for Lorentz and polarization effects. Equivalent reflections were merged, and semiempirical absorption corrections were made. Space group, lattice parameters and other relevant information for the structure are given in Table 1. The structure was solved by direct methods with full-matrix least-squares refinement, employing the NRCVAX package.[23−28] All non-hydrogen atoms were refined with anisotropic thermal parameters. The final structure is reasonably well ordered, although the C atom of the SCN moiety has odd thermal parameters. It was not possible to locate the H atoms, and only those which could be calculated with confidence were included in the final model. The final difference electron density map for the S-bound isomer was very noisy, with several peaks around the Re position.

Results and Discussion

Syntheses. The boronic acid capped technetium(III) tris(dioxime) complexes (BATOs) were prepared by template synthesis by substitution and reduction of TcO_4^- in the presence of excess thiocyanate. This method is similar to that previously reported for the BATO complexes with chloride or bromide in the seventh coordination site.[8,9] However, the NCS/SCN reaction was halted without maximizing yields in order to isolate the thiocyanato-BATO. Although the thiocyanato- and isothiocyanato-BATOs are generated simultaneously, the thermodynamically less stable thiocyanato-BATO readily isomerizes to the isothiocyanato analogue in solution, a light catalyzed reaction. The two linkage isomers are easily separated by silica gel chromatography with the more lipophilic isothiocyanate isomer eluting first. By reversed phase HPLC chromatographic analysis, the order of elution is reversed with the less hydrophobic thiocyanate isomer eluting earlier. The thiocyanato-BATO is red-brown in color, while the isothiocyanato-BATO is ruby red. Over time and exposure to light, the thiocyanate analogue isomerizes to the isothiocyanate analogue in solution in the absence of water. If water is present, the thiocyanate analogue undergoes both S to N linkage isomerization and hydrolysis to the hydroxy-BATO. The latter reaction is pH dependent, occurring above pH ca. 6.[12]

Syntheses of the hydroxy BAReO and the thiocyanato and isothiocyanato BAReO complexes were not as straightforward as those for other analogues with different anions coordinated in the seventh coordination site. The hydroxy BAReO, ReOH(CDOH)$_2$(CDO)BMe, was synthesized by a ligand exchange reaction onto the chloro-substitued analogue. The hydroxy complex showed particular pH sensitivity, decomposing under acidic conditions in which its Tc analogue was reported to be stable.[12] In addition, the Cl → OH substitution was complicated by multiple products at pH > 8. Both the thiocyanato and the isothiocyanato linkage isomers were formed in the reaction of SCN^- with the hydroxy-BAReO under acidic conditions. Under neutral to basic conditions, the reaction was not efficient, consistent with a mechanism involving protonation of the OH and subsequent loss of H_2O to generate a transient 6-coordinate intermediate followed by SCN/NCS substitution.[12] Both isomers were observed by HPLC and TLC. However, isolation of the thiocyanate isomer proved difficult because of the low yield of the reaction and the SCN to NCS linkage isomerization. As for the Tc congeners, this isomerization was seen to be catalyzed by light. To isolate the thiocyanato complex, reactions and separations were carried out in the dark and at room temperature. Higher temperatures, which would have increased the rate of substitution of the seventh ligand, increased the S to N isomerization reaction. Thus, only a very small quantity of the thiocyanato isomer was isolated (ca. 1.3%). This quantity of material proved sufficient for an X-ray structure determination, HPLC analysis, and ^{1}H NMR, FT-IR, and UV−visible spectral characterization. Reversed phase HPLC analysis of the Re linkage isomers was similar to that observed for the analogous Tc complexes, with the thiocyanate isomer eluting shortly before the isothiocyanate isomer. A higher yield was

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(25) Scattering factors, including f' and f'', were taken from the *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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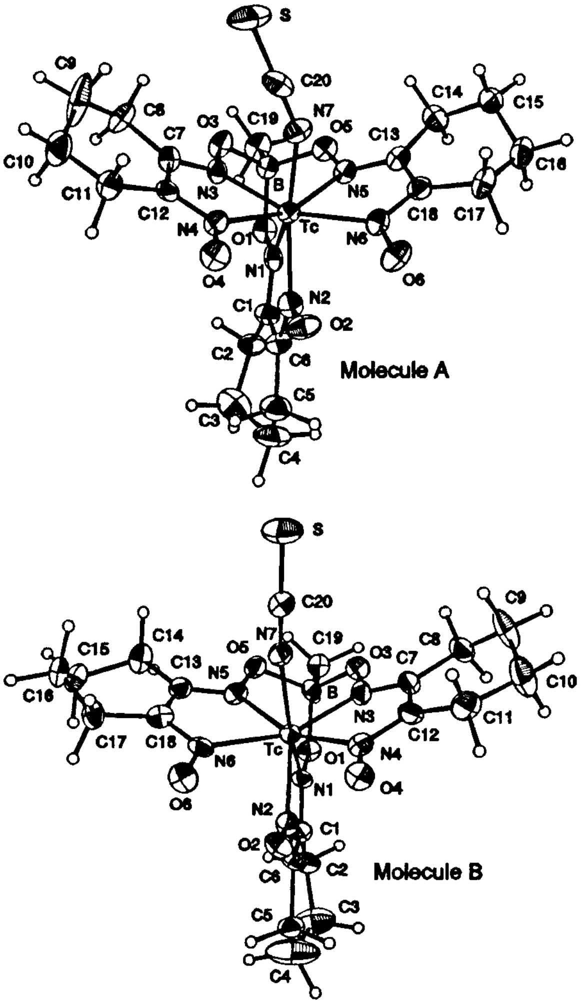

Figure 1. ORTEP representation of both molecules of [TcNCS-(CDOH)$_2$(CDO)BMe] showing 50% probability elipsoids. Two independent molecules were observed in the unit cell.

achieved for the Tc−SCN complex because of the more favorable synthetic route and the more facile substitution on Tc.

Characterization. The FT-IR spectra of the various Re and Tc complexes showed the expected C=N stretches in the 1550−1650 cm^{-1} range, the N−O stretches in the ranges 950−1160 and 1190−1210 cm^{-1}, and the B−O stretches at ca. 810−820 and 1045−1225 cm^{-1}.[1] The NCS$^-$- and SCN$^-$-substituted analogues exhibited their C≡N stretch in the range of 2055−2079 cm^{-1} for the N-bound isomer and 2114−2124 cm^{-1} for the S-bound isomer. These assignments are consistent with N- and S-bound NCS$^-$ moieties observed for other transition metal complexes.[30] The C≡N stretch observed for the N-bound linkage isomers is in the range observed for other Tc[31−35] and Re[36−43] isothiocyanate complexes.

The ^{1}H NMR spectra for the various BATO and BAReO complexes are similar and consistent with the proposed formulations. Broad multiplets (integrating for 24H) are observed between 1.6 and 3.4 ppm for the cyclohexyl methylene protons. The protons on the carbon adjacent to the boron are shielded such that they are observed very close to TMS (0.1−0.7 ppm). The bridging oxime protons are observed at ca. 15 ppm. These protons appear as a sharp singlet and this position is most clearly affected by the identity of the seventh ligand. Although the position of the methyl group is also affected by the seventh ligand, its proximity to TMS and vacuum grease (just downfield of TMS) made it less reliable. The proton-decoupled ^{13}C NMR spectra showed the alkyl C signals for the CDO ligands between 20 and 30 ppm, the oxime C signals between 145 and 162 ppm, and the β-C on the BEt cap at less than 8.27 ppm. The C bound directly to boron and the isothiocyanato C were not observed.

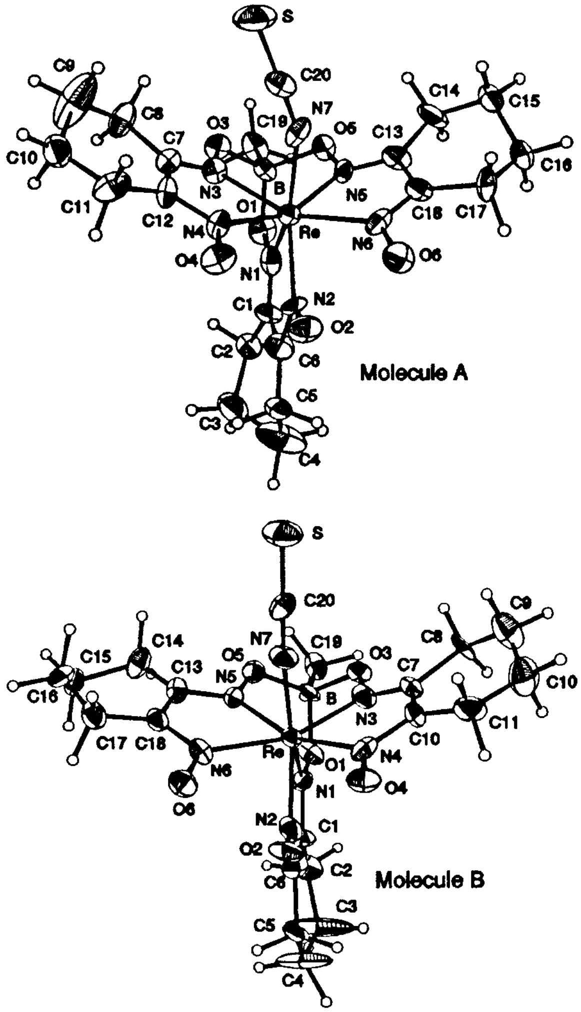

Figure 2. ORTEP representation of both molecules of[ReNCS-(CDOH)$_2$(CDO)BMe] showing 50% probability elipsoids. Two independent molecules were observed in the unit cell.

Deuterium NMR spectroscopy of ReOD(CDOH)$_2$(CDO)-BMe•D$_2$O in CH$_2$Cl$_2$ showed that the Re−OD and the hydrogen

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg)

	$\mathrm{ReNCS(CDOH)_2(CDO)BMe}$		$\mathrm{TcNCS(CDOH)_2(CDO)BMe}$		
	molecule a	molecule b	molecule a	molecule b	$\mathrm{ReSCN(CDOH)_2(CDO)BMe}$
M−N1	2.06(2)	2.09(1)	2.05(1)	2.06(1)	2.05(1)
M−N2	2.05(1)	2.08(2)	2.07(1)	2.07(1)	2.06(1)
M−N3	2.09(1)	2.04(2)	2.026(9)	2.04(1)	2.07(1)
M−N4	2.11(1)	2.10(2)	2.10(1)	2.11(1)	2.09(1)
M−N5	2.03(1)	2.08(1)	2.06(1)	2.04(1)	2.07(2)
M−N6	2.11(2)	2.17(1)	2.12(1)	2.15(1)	2.11(1)
M−N7	2.08(2)	2.08(1)	2.11(1)	2.07(1)	
M−S					2.453(4)
N7−C20	1.17(3)	1.13(3)	1.13(2)	1.14(2)	1.19(4)
S−C20	1.58(3)	1.61(2)	1.62(2)	1.63(2)	1.68(3)
N1−M−N2	71.9(6)	72.4(6)	70.6(4)	70.2(4)	72.5(6)
N1−M−N3	77.6(6)	77.9(6)	77.0(4)	79.5(4)	77.6(5)
N1−M−N4	112.6(6)	115.2(6)	111.9(4)	114.2(4)	113.1(6)
N1−M−N5	81.9(6)	75.2(6)	79.7(4)	78.3(4)	77.4(6)
N1−M−N6	117.7(6)	112.1(6)	115.7(4)	111.4(4)	114.3(5)
N1−M−N7	151.4(7)	152.1(7)	153.8(4)	153.7(4)	
N1−Re−S					153.4(4)
N2−M−N3	125.7(6)	122.2(6)	122.8(4)	123.6(4)	123.0(5)
N2−M−N4	78.0(6)	76.2(7)	77.3(4)	77.2(4)	76.9(5)
N2−M−N5	125.4(6)	123.5(6)	124.1(4)	124.2(4)	123.4(5)
N2−M−N6	78.3(7)	77.0(6)	79.1(4)	76.8(4)	77.8(5)
N2−M−N7	136.6(7)	135.5(7)	135.5(4)	136.1(4)	
N2−M−S					133.7(4)
N3−M−N4	73.8(5)	73.4(7)	72.9(4)	73.6(5)	72.0(5)
N3−M−M5	92.3(6)	93.7(7)	93.4(4)	92.8(5)	94.7(5)
N3−M−N6	155.8(7)	160.8(6)	158.1(4)	159.6(4)	159.2(6)
N3−M−N7	80.8(7)	84.0(6)	83.7(4)	83.7(4)	
N3−M−S					81.7(4)
N4−M−N5	156.3(6)	160.3(6)	158.6(4)	158.5(4)	159.7(6)
N4−M−N6	112.7(6)	113.8(6)	114.6(4)	114.4(4)	115.0(5)
N4−M−N7	78.5(7)	78.9(7)	78.4(4)	79.6(4)	
N4−M−S					75.4(4)
N5−M−N6	72.9(7)	74.1(6)	72.8(4)	73.5(4)	72.6(5)
N5−M−N7	80.5(7)	85.1(7)	84.0(4)	82.5(4)	
N5−M−S					87.9(4)
N6−M−N7	78.0(6)	80.3(6)	78.1(4)	79.6(4)	
N6−M−S					81.4(4)
M−N7−C20	155.5(17)	166.8(17)	148.5(11)	167.5(10)	
M−S−C20					112.2(6)
N7−C20−S	178(2)	179(2)	176(1)	179(1)	175(3)

bonded D_2O were observed as a singlet at 1.85 ppm. The D_2O is assigned as hydrogen bonded because, in the absence of this complex, D_2O in CH_2Cl_2 is observed at 1.52 ppm. The ^{2}H NMR experiments confirm the assignments in the ^{1}H NMR spectrum of this complex in which the Re−OH and the H_2O are observed in the cyclohexyl methylene multiplets between 1.6 and 1.85 ppm. Their presence is suggested by integration (15H rather than 12H). Elemental analysis results are consistent with the presence of a water of hydration.

Molecular ions were observed for [$\mathrm{TcNCS(CDOH)_2(CDO)BMe}$] and [$\mathrm{TcSCN(CDOH)_2(CDO)BMe}$] in their FAB mass spectra at *m*/*z* 606, and the loss of the NCS group was observed at *m*/*z* 547. The analogous species were observed in the FAB mass spectrum for [$\mathrm{ReNCS(CDOH)_2(CDO)BEt}$] at *m*/*z* 706 for the molecular ion and at *m*/*z* 648 for the loss of the NCS moiety.

Linkage Isomerization. The linkage isomerization reaction of the Tc thiocyanate complex exhibited four isosbestic points in CH_2Cl_2 (355, 372, 432, and 462 nm), consistent with the direct conversion to a single product. HPLC analysis of the reaction in progress confirmed the clean conversion of the thiocyanate to the isothiocyanate complex. A half-life for the isomerization 10−12 h (25 °C) was estimated from the spectral and HPLC experiments.[22] The same reaction for the Re thiocyanate complex proved to be too slow to measure (no change over 1 month at ∼25 °C in $CHCl_3$ or CH_3CN). Similar to the Tc complexes, however, the isomerization was accelerated by light, with half-lives of ca. 75 and ca. 0.3 h in $CHCl_3$ and CH_3CN, respectively.

NCS/SCN−OH Exchange Reaction. The rate of conversion of $^{99m}\mathrm{Tc(NCS/SCN)(CDOH)_2(CDO)BMe}$ to $^{99m}\mathrm{TcOH(CDOH)_2(CDO)BMe}$ (pH 8.0 phosphate buffer, 37 °C) was determined by HPLC analysis. The individual rates of the hydrolyses of the linkage isomers were not separable. The overall pseudo-first-order rate constant was 1.3×10^{-4} s^{-1} ($t_{1/2} = 3.1$ h), significantly slower than the hydrolysis of the chloride analogue, $^{99m}\mathrm{TcCl(CDOH)_2(CDO)BMe}$, which had a half-life of ca. 6 min.[12]

Crystallography. The X-ray crystal structures of the N-bound isothiocyanato complexes, $\mathrm{ReNCS(CDO)_2(CDOH)BMe}$ and $\mathrm{TcNCS(CDO)_2(CDOH)BMe}$, showed them to be isomorphic with both crystallizing in the space group $P2_12_12_1$. The ORTEP[44] representations of $\mathrm{TcNCS(CDOH)_2(CDO)BMe}$ and $\mathrm{ReNCS(CDOH)_2(CDO)BMe}$ are shown in Figures 1 and 2, respectively. Selected bond lengths and bond angles are listed in Table 2. The X-ray crystal structure determination of the S-bound thiocyanato complex, $\mathrm{ReSCN(CDOH)_2(CDO)BMe}$, was made difficult by the crystal habit. The crystals grew as very thin plates in clusters and were so brittle that a single crystal

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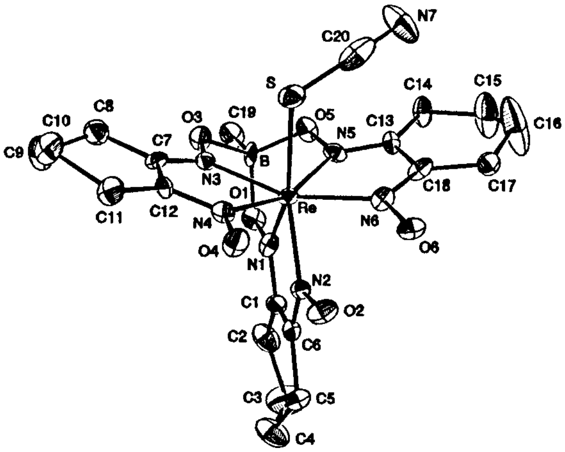

Figure 3. ORTEP representation of [ReSCN(CDOH)$_2$(CDO)BMe] showing 50% probability elipsoids.

could not be broken from the clusters without shattering. The data were collected on a fragment less than 0.01 mm thick which was not completely single. While these data were sufficient for determining the structure, the refinement parameters were poor and the final difference map was noisy. The ^{1}H NMR spectrum of crystals of the S-bound isomer showed a small impurity of the N-bound isomer as did the HPLC analysis (ca. 7%). The ORTEP[44] representation of ReSCN(CDOH)$_2$(CDO)-BMe is shown in Figure 3. Selected bond lengths and bond angles are listed in Table 2.

The metal−dioxime nitrogen bond lengths in the structures reported here (av Re−N, 2.081 Å; av Tc−N, 2.074 Å) are consistent with those previously reported for BATO[8,9] (2.037−2.14 Å) and BAReO[7] (2.028−2.108 Å) complexes. The M−N distances are, on average, shorter on the boron-capped end than on the uncapped end, by about 0.035−0.06 Å. Although the ^{1}H NMR spectra of these complexes showed two hydrogen-bonded oxime protons per molecule (vide infra), they could not be unequivocally identified in the two crystal structures and therefore are not included in any of the ORTEP representations or Table 2. In previously reported BATO[8,9] and BAReO[7] structures, the hydrogen-bonded oxime protons were located from the electron density maps.

The M−NCS distances observed in the complexes are 2.09(2) Å for Tc and 2.10(2) Å for Re. There have been relatively few Tc[31−35] or Re[36−43] structures reported with coordinated NCS$^-$ groups. The five Tc structures having a coordinated isothiocyanate group showed Tc−N bond distances ranging from 2 to 2.162 Å, but for the one Tc(III) complex the Tc−NCS bond distances reported are 2.04−2.05 Å.[31−35] The ten Re structures reported with a coordinated isothiocyanate group showed Re−N bond distances ranging from 1.941 to 2.257 Å.[36−43] However, the 7-coordinate Re(III) structure, [ReNCS(terpy)$_2$]$^{2+}$, exhibited a 2.046(9) Å bond distance.[42]

The Re−SCN distance observed is 2.453(4) Å, which is significantly longer (0.35 Å) than the M−NCS distances reported. This is consistent with the difference in other M−NCS and M−SCN distances reported,[45] and is close to the Re−Cl distance reported for the analogous BAReO complexes.[7] For analogous Co(III) complexes, the Co−SCN bond distances are 0.35−0.36 Å longer than the Co−NCS distances.[14] The bond angles about the coordinated N or S are also indicative of the mode of coordination. M−N−C bond angles are always close to linear while M−S−C bond angles are bent and close to 110°.[14] The average bond angle observed for the N-bound structures reported here is 160°, while the bond angle observed for the S-bound analogue was found to be 112.2°.

Conclusion

Both linkage isomers, MNCS and MSCN, were observed for the Tc(III) and Re(III) 7-coordinate monocapped tris(dioxime) complexes. The N-bound isothiocyanato complex was found to be the more thermodynamically stable linkage isomer in all cases and the kinetics of the linkage isomerization could be readily monitored. This finding is consistent with Jorgensen's theory of "symbiotic ligands": the six "hard" imine nitrogens favor the coordination of the "hard" isothiocyanate nitrogen in preference to the "soft" thiocyanate sulfur.[46] Our results are consistent with the only other 7-coordinate Tc(III) or Re(III) complex in which N-bound isothiocyanate is observed with six "hard" terpy nitrogens bound to Re(III).[42] The use of controlled reaction conditions (low temperature, minimal exposure to light, short reaction time) were used to allow the isolation and identification of the unfavored S-bound thiocyanate linkage isomers [MSCN(CDOH)$_2$(CDO)BMe] (M = Tc, Re). The formation of the thermodynamically unfavored MSCN isomer is driven by a kinetic effect in that the mechanism of ligand exchange (M−OH + SCN$^-$) favors the better nucleophile, thiocyanate. This is the first report, to our knowledge, of S-bound thiocyanate coordinated to Tc or Re in any oxidation state.

Acknowledgment. We gratefully acknowledge the support provided from the National Science Foundation NSF CHE 9011804 (X-ray facility) and 8908304 (500 MHz NMR).

Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available on the Internet only. Ordering information is given on any current masthead page.

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