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Synthesis and Characterization of Rhenium(V) Oxo Complexes with a New Thiol−Amide−Thiourea Ligand System. X-ray Crystal Structure of [1-Phenyl-3-[2-((2-thioacetyl)amino)ethyl]thioureato]oxorhenium(V)

Malgorzata Lipowska,[†] Lory Hansen,[†] Andrew Taylor, Jr.,[†] and Luigi G. Marzilli*,[‡]

Departments of Radiology and Chemistry, Emory University, Atlanta, Georgia 30322

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General methods for preparing $Re^{V}O$ complexes with a novel series of thiol−amide−thiourea (TATU) ligands, a new class of N_2S_2 chelates, were developed. The TATU ligands, the first multidentate systems designed with a bidentate thiourea moiety, have been used to prepare the first high-valent transition metal complexes with bidentate thiourea coordination. Direct reaction of *N*-(2-aminoethyl)-2-((triphenylmethyl)thio)acetamide (**1**) with phenyl, 4-methoxyphenyl, 4-chlorophenyl, and methyl isothiocyanate afforded ready access to the corresponding S-protected TATU ligands in one step. A two-step preparation of the *N,N*-dimethylthiourea TATU ligand derived from **1** was also developed. Deprotection of thiols in trifluoroacetic acid with triethylsilane followed by a ligand exchange reaction with $Re^{V}O$ precursors yielded neutral ReO(TATU) complexes. The structure of [1-phenyl-3-[2-((2-thioacetyl)amino)ethyl]thioureato]oxorhenium(V) (**6a**) was determined by X-ray diffraction methods. Crystal data for **6a**: $C_{11}H_{12}N_3O_2ReS_2$, fw 468.6, orthorhombic, $Pca2_1$; $a = 22.605(5)$ Å, $b = 13.029(3)$ Å, $c = 9.698(2)$ Å; $V = 2856.3(11)$ Å^3; Z = 8. The coordination environment of **6a** was pseudo-square-pyramidal with a deprotonated thiol S, deprotonated amide N, deprotonated thiourea N, and thiocarbonyl S coordinated in the basal plane and the oxo ligand in the apical position. The thiourea function forms a four-membered chelate ring in the multidentate TATU ligands. The two N−C and the S−C bond distances within the monodeprotonated thiourea moiety were typical of bonds with multiple-bond character. Solution ^{1}H NMR data for all five complexes were consistent with the solid-state structure of **6a.** A broad singlet attributable to the uncoordinated NH group of thiourea was observed for the monosubstituted thiourea complexes but was not present for the *N,N*-dimethylthiourea derivative. Instead, two singlets of equal intensity were observed for the two methyl groups, indicating that there is restricted rotation around the $C{-}N(CH_3)_2$ bond and an extended π system in the thiourea moiety. The four-membered ring might cause difficulty because the M−S distance would be relatively long in an undistorted ligand. This may be the reason such chelate ligands have not been previously investigated. However, the N−C−S angle narrows to ~105°, permitting a Re−S bond with a typical bond length to be formed. We conclude that such a ring represents a versatile new building block to create multidentate ligands.

Introduction

There is much interest in the use of MN_2S_2 complexes as diagnostic imaging and radiotherapeutic agents (M = Tc(V), Re(V))[1] and as structural, spectroscopic, and functional models of metal sites in metalloproteins (M = Cu, Ni, Zn, Mo).[2−5] Thiourea and its derivatives (tu) are common ligands in transition metal chemistry, including Tc and Re chemistry. In the preparation of complexes with Tc and Re from $[M^{VII}O_4]^-$ salts, thiourea acts as both reducing agent and ligand[6−9] and, as a ligand, is easily replaced under mild conditions. Therefore, $[Tc(tu)_6]^{3+}$ ions have often been used as starting materials for low-valent and mixed-ligand Tc complexes.[10,11] The thiourea ligands usually coordinate through the sp^2-hybridized sulfur in a monodentate manner; however, they have three potential donor sites, the S and two (deprotonated) N atoms. Only a few examples of bidentate thiourea coordination through sulfur and one deprotonated nitrogen have been reported.[11−15] *N*-(*N,N*-dialkylthiocarbamoyl)benzamidines are bidentate ligands that contain a N−C(=S)−N fragment, but they coordinate through the thiocarbonyl and a terminal primary amine, forming a six-membered chelate ring.[16] Bidentate thiopyrimidine derivatives are also known.[17−19] However, *N*-(*N,N*-dialkylthiocarbamoyl)-

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[†] Department of Radiology

[‡] Department of Chemistry

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benzamidines and thiopyrimidines are chemically dissimilar from thioureas.

There is a versatile organic chemistry that would allow the thiourea function to be built into a wide range of chelate ligands. As part of our research in the design of new Tc and Re complexes with novel ligand systems, we successfully synthesized and characterized a series of thiol−amide−thiourea TATU (N_2S_2) ligands and their Re(V) oxo complexes. The ligands are the first multidentate systems designed with a bidentate thiourea moiety. The Re^VO complexes represent the first high-valent transition metal species in which bidentate coordination of a thiourea moiety has been confirmed by X-ray diffraction methods. The four-membered chelate ring could have presented problems, since in an undistorted geometry the Re−S distance would be long. However, distortions in this four-membered chelate ring permit normal M−S distances to form.[20]

Experimental Section

N-(2-Aminoethyl)-2-((triphenylmethyl)thio)acetamide[20] (**1**), $ReOCl_3(Me_2S)(OPPh_3)$,[21,22] and $ReO_2I(PPh_3)_2$[23] were prepared as described previously. Isothiocyanates **3a**−**d** and all other reagents and solvents were obtained from Aldrich and used as received. Air-sensitive reactions were carried out under a nitrogen atmosphere. Column chromatography was conducted on Merck silica gel 60 (230−400 mesh ASTM). Thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254} plates developed in 5% $MeOH/CHCl_3$ and visualized by UV illumination at 254 nm and/or by iodine reagents. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. ^1H NMR spectra, recorded on a General Electric QE-300 spectrometer, were referenced to internal TMS. The FT IR spectra (KBr pellet) were recorded with a Nicolet 510M instrument. Melting points are uncorrected.

***N*-(2-Isothiocyanatoethyl)-2-((triphenylmethyl)thio)acetamide (2).** Thiophosgene (0.46 g, 0.30 mL, 4 mmol) was introduced slowly through a syringe into a stirred mixture of **1** (0.75 g, 2 mmol) and Na_2CO_3 (0.53 g, 5 mmol) in dry $CHCl_3$ (20 mL) at 0 °C under N_2. The reaction mixture was stirred at room temperature for 1 h and filtered. The filtrate was washed with water and dried over anhydrous $MgSO_4$. The solution was concentrated on a rotary evaporator, and the oily residue was purified by column chromatography (silica gel, 1−5% $MeOH/CHCl_3$) to give 0.52 g (62%) of **2**: mp 130−131 °C.

Preparation of Ligands. General Procedure for Compounds 4a−d. To a solution of **1** (0.4 mmol) in EtOH (20 mL) was added the appropriate isothiocyanate **3a**−**d** (0.4 mmol). The reaction mixture was stirred at room temperature for 1−3 h until TLC monitoring indicated complete conversion of **1**. Evaporation of solvent was followed by chromatography (silica gel, 1−5% $MeOH/CHCl_3$) and recrystallization from EtOH.

1-Phenyl-3-[2-((2-((triphenylmethyl)thio)acetyl)amino)ethyl]thiourea (4a): 98%; mp 163−164 °C.

1-(4-Methoxyphenyl)-3-[2-((2-((triphenylmethyl)thio)acetyl)amino)ethyl]thiourea (4b): 91%; mp 178−179 °C.

1-(4-Chlorophenyl)-3-[2-((2-((triphenylmethyl)thio)acetyl)amino)ethyl]thiourea (4c): 82%; mp 192 °C.

1-Methyl-3-[2-((2-((triphenylmethyl)thio)acetyl)amino)ethyl]thiourea (**4d**): 62%; mp 173−174 °C.

1,1-Dimethyl-3-[2-((2-((triphenylmethyl)thio)acetyl)amino)ethyl] thiourea (4e). Dimethylamine in methanol (2 M, 0.25 mL, 0.5 mmol) was added dropwise to the isothiocyanate **2** (0.209 g, 0.5 mmol) in 20 mL of methanol. The reaction mixture was stirred at room temperature for 2 h. The resulting white solid was collected, washed with cold methanol, and dried in vacuo. Crystallization from methanol gave **4e** in 80% yield; mp 192 °C.

General Procedure for Compounds 5a−e. Triethylsilane (1.4 mmol) was added slowly to a solution of **4** (1.3 mmol) in trifluoroacetic acid (5 mL). The reaction mixture was partitioned between hexane (5 mL) and water (10 mL). The aqueous layer was removed, washed with hexane, and filtered through Celite. Removal of solvent under reduced pressure gave a clear oil, which was recrystallized from ethanol/ether to give analytically pure **5**.

1-Phenyl-3-[2-((2-thioacetyl)amino)ethyl]thiourea (5a): 89%; mp 119−120 °C.

1-(4-Methoxyphenyl)-3-[2-((2-thioacetyl)amino)methyl]thiourea (5b): 88%; mp 162−163 °C.

1-(4-Chlorophenyl)-3-[2-((2-thioacetyl)amino)ethyl]thiourea (5c): 93%; mp 170−171 °C.

1-Methyl-3-[2-((2-thioacetyl)amino)ethyl]thiourea (**5d**): 88%; (oil).

1,1-Dimethyl-3-[-2-((2-thioacetyl)amino)ethyl]thiourea (5e): 96%, (oil).

Preparation of Complexes. General Procedure for Compounds 6a−d. To a stirred solution of ligands **5a**−**d** (0.7 mmol) in MeOH (40 mL) was added 1 N NaOAc in MeOH (8 mL), followed by solid $ReOCl_3(Me_2S)(OPPh_3)$ (0.75 mmol). The reaction mixture was heated to 80 °C for 2 h and then cooled to room temperature. The mixture was diluted with EtOAc (50 mL), washed three times with water, and dried over $MgSO_4$. Concentration of the organic layer was followed by chromatography (silica gel, 1−10% $MeOH/CHCl_3$) and then crystallization from EtOH to give analytically pure samples of **6a**−**d**.

[1-Phenyl-3-[2-((2-thioacetyl)amino)ethyl]thioureato]oxorhenium(V) (6a): 65%.

[1-(4-Methoxyphenyl)-3-[2-((2-thioacetyl)amino)ethyl]thioureato]oxorhenium(V) (6b): 72%.

[1-(4-Chlorophenyl)-3-[2-((2-thioacetyl)amino)ethyl]thioureato]oxorhenium(V) (6c): 86%.

[1-Methyl-3-[2-((2-thioacetyl)amino)ethyl]thioureato]oxorhenium(V) (6d): 51%.

[1,1-Dimethyl-3-[2-((2-thioacetyl)amino)ethyl]thioureato]oxorhenium(V) (6e). Compound **6e** was prepared in a similar manner from **5e** (0.05 g, 0.23 mmol) and $ReO_2I(PPh_3)_2$ (0.196 g, 0.23 mmol). Red needles were obtained in 58% yield from EtOH.

X-ray Crystallography. A red crystal of **6a** with dimensions of 0.22 × 0.28 × 0.12 mm was used for data collection. Intensity data were collected at room temperature on a Siemens P4 instrument. The crystal system and high-angle cell constants were determined by automatic reflection selection, indexing, and least-squares refinement (XSCANS Version 2.0). Three check reflections were measured every 97 reflections; there was no significant deviation in intensity. Intensity data were corrected for Lorentz and monochromator polarization and absorption (semiempirical method based on azimuthal scans). The structure of **6a** was successfully solved by Patterson methods and refined by full-matrix least-squares procedures on F^2 using SHELXL 93 in the noncentrosymmetric space group $Pca2_1$ but not in the centrosymmetric space group *Pbcm*. The absolute configuration was determined from the Flack *x* parameter (calculated for each configuration).[24,25] N, O, Re, and S atoms were refined anisotropically. The carbon atoms were refined isotropically in order to maintain an acceptable data to parameter ratio. H atoms were generated at calculated positions ($d(C-H) = 0.96$ Å, $d(N-H) = 0.90$ Å) and constrained using a riding model with isotropic thermal parameters that were 20% greater than the *U*(eq) of the atom to which they were bonded. Crystal data and refinement parameters are presented in Table 1.

Results and Discussion

Synthetic Chemistry. *N*-(2-Aminoethyl)-2-((triphenylmethyl)thio)acetamide (**1**) is a known ligand precursor for the synthesis of the diamide−thiol−thioether[20] (N_2S_2) and diamide−

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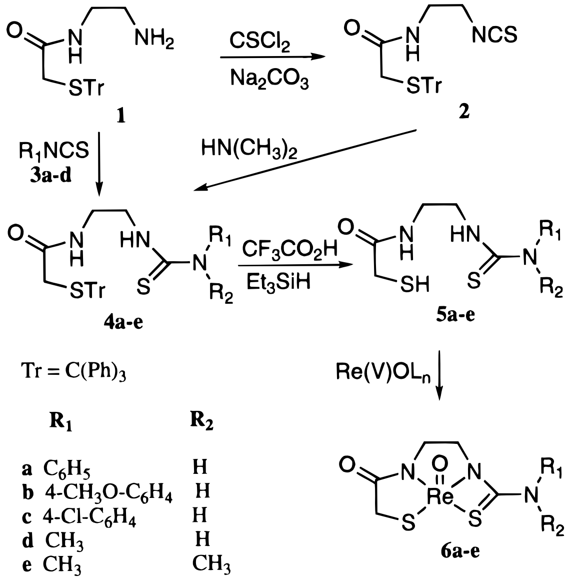
Table 1. Crystallographic Data for **6a**

empirical formula	$C_{11}H_{12}N_3O_2ReS_2$
crystal system	orthorhombic
space group	$Pca2_1$
a (Å)	22.605(5)
b (Å)	13.029(3)
c (Å)	9.698(2)
V (Å^3)	2856.3(11)
Z	8
fw	468.56
d (calc) (mg/m^3)	2.18
abs coeff (mm^{-1})	8.80
radiation (λ (Å))	Mo Kα (0.7103)
temp (K)	293(2)
min./max transm	0.008/0.038
final R indices [$I > 2\sigma(I)$]	R1 = 0.040, wR2 = 0.096
R indices (all data)	R1 = 0.045, wR2 = 0.099

Scheme 1



thiol−pyridine[26] (N_3S) $^{99}Tc^{V}O$ complexes which were designed in the development of technetium-99m radiopharmaceuticals. The importance of this precursor lies in the presence of the three potential donor sites, the sulfur atom and two nitrogen atoms. The terminal primary amine can be used to extend the ligand by methods common to peptide synthesis, namely the use of activated esters and coupling reagents for the formation of amide bonds.[27]

Primary amines also react rapidly with the isothiocyanate group to form a stable thiourea linkage. This approach was used for the straightforward preparation of a new series of thiol−amide−thiourea N_2S_2 (TATU) ligands according to the route shown in Scheme 1. This is a versatile approach for the synthesis of thiourea chelate ligands since a variety of isothiocyanate agents are commercially available and many amine precursors can be used to construct polydentate ligands. Five new TATU ligands prepared by this route along with their $Re^{V}O$ complexes are reported here. The reactions of amine **1** with appropriate isothiocyanates **3a**−**d** (Scheme 1) were performed in ethanol solution at room temperature and gave thiourea ligands **4** in very good yields (82−98%) for the aryl derivatives (**4a**−**c**) and in moderate yield (62%) for the alkyl derivative (**4d**).

The variety of TATU ligands that may be prepared can be greatly increased by conversion of the primary amine **1** to isothiocyanate **2** and then treatment of **2** with an amine. The synthesis of the *N*,*N*-dimethylthiourea derivative **4e** is a successful example of this approach. This route is given in Scheme 1. **1** was treated with thiophosgene in the presence of sodium carbonate to furnish the isothiocyanate derivative **2** in moderate yield (62%). Compound **2** gave a strong infrared absorption at 2100 cm^{-1}, characteristic of the isothiocyanate function. Treatment of **2** with a methanol solution of dimethylamine gave the expected *N*,*N*-dimethylthiourea derivative **4e** in good yield (80%).

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for **6a**

atom	x	y	z	U(eq)[a]
Re(1)	9684(1)	9591(1)	10000	57(1)
S(1)	9222(2)	8662(4)	11660(6)	64(1)
S(2)	9382(2)	11258(3)	10814(6)	59(1)
O(1)	9401(6)	9355(11)	8400(16)	82(4)
O(2)	10767(4)	7288(9)	11579(15)	76(4)
N(1)	10370(5)	8681(10)	10456(18)	61(5)
N(2)	10370(5)	10576(10)	10084(22)	62(4)
N(3)	10470(5)	12228(10)	11012(16)	56(4)
C(1)	9745(6)	7570(16)	11851(21)	70(5)
C(2)	10347(7)	7843(14)	11276(19)	57(4)
C(3)	10940(6)	9024(12)	9854(23)	66(4)
C(4)	10978(6)	10208(11)	10151(18)	51(4)
C(5)	10141(6)	11417(13)	10579(18)	56(4)
C(6)	10266(6)	13085(13)	11758(17)	51(4)
C(7)	10619(8)	13430(15)	12822(20)	70(5)
C(8)	10446(8)	14312(15)	13521(22)	72(5)
C(9)	9929(9)	14827(16)	13168(23)	70(5)
C(10)	9590(8)	14455(15)	12098(21)	62(5)
C(11)	9771(6)	13602(14)	11375(18)	56(4)
Re(2)	2240(1)	4814(1)	4763(1)	49(1)
S(3)	1745(2)	3620(3)	6013(5)	57(1)
S(4)	1912(2)	6297(3)	5979(6)	65(1)
O(3)	1989(5)	4812(10)	3110(15)	75(4)
O(4)	3298(4)	2292(9)	5634(17)	91(5)
N(4)	2919(4)	3884(8)	5055(16)	47(3)
N(5)	2907(5)	5765(8)	5157(16)	55(4)
N(6)	2990(5)	7269(10)	6531(17)	61(4)
C(12)	2236(6)	2540(15)	5815(22)	75(5)
C(13)	2866(7)	2886(13)	5485(19)	60(4)
C(14)	3502(6)	4305(11)	4715(23)	56(4)
C(15)	3528(6)	5433(12)	5186(21)	59(4)
C(16)	2681(6)	6545(12)	5873(17)	50(4)
C(17)	2771(6)	8184(12)	7177(16)	45(4)
C(18)	3152(8)	8682(16)	8075(21)	76(6)
C(19)	2985(8)	9581(15)	8619(22)	74(5)
C(20)	2443(8)	10035(14)	8351(20)	61(4)
C(21)	2067(9)	9534(17)	7469(22)	79(6)
C(22)	2237(8)	8621(15)	6851(22)	71(5)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

In all reactions, S-protected thiourea derivatives **4** were the major product and purification of ligands **4a**−**e** was simple. Column chromatography to remove the polymeric materials and then crystallization from ethanol produced compounds of high purity. The spectroscopic and analytical data obtained for these protected ligands were consistent with the structures shown. The simplicity and efficiency of the preparation of these compounds indicate that these N_2S_2 thiourea chelates represent a new class of readily prepared, versatile ligands.

The free thiol ligands were cleanly isolated by dissolving the *S*-triphenylmethyl (STr) protected derivatives **4** in trifluoroacetic acid, titrating the deep yellow Tr^+ cation with triethylsilane until the solution was colorless, extracting with hexane (to remove TrH), and evaporating the solvent. The proposed structures of the resulting ligands **5** in Scheme 1 were supported by the analytical and ^1H NMR spectral data.

$Re^{V}O$ complexes **6a**−**d** of TATU ligands **5a**−**d** were prepared by ligand exchange of $ReOCl_3(Me_2S)(OPPh_3)$ in basic

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methanol solution (Scheme 1). Ligand **5e** was transformed into **6e** in the same manner, except $ReO_2I(PPh_3)_2$ was used as the Re^VO precursor. These precursors can be used interchangeably with the TATU ligands with very good results. Direct reduction of TcO_4^- with $SnCl_2$ in the presence of TATU ligands under basic conditions was effective; however, this procedure did not work for ReO_4^-, which is more difficult to reduce than TcO_4^-.[28−30] Furthermore, all ligand exchange reactions were performed in organic solvent, which facilitated isolation of resulting neutral metal−oxo chelates **6a**−**e** by silica gel chromatography. The R_f values on silica gel TLC were consistent with the high lipophilicity of these compounds. Complexes **6a**−**e**, which were air-stable solids, soluble in polar organic solvents, were characterized by analytical and spectroscopic data (see Supporting Information).

NMR Spectroscopy. In the ^1H NMR spectra of the ReO(TATU) complexes there was a pair of doublets at ∼3.6 ppm and 4.15 ppm (J = 17 Hz), each integrating to one proton. The coupling constant (J(AB) = ∼17 Hz) was similar to those reported by Bryson et al.[20,26] for the SCH_2 splitting in related complexes. The NCH_2CH_2N unit appeared as a set of four multiplets (ABCD pattern). These resonances are characteristic of $ReO(N_2S_2)$ and $ReO(N_3S)$ complexes with ligands derived from **1**. The spectra of **6a**−**e** did not exhibit the triplet at ∼2.00 ppm that was assigned to the thiol proton of the free ligands. A characteristic feature in the spectra of the ReO(TATU) complexes **6a**−**d** was a broad singlet at ∼10 ppm integrating to one proton. The signal was exchangeable with that of deuterium oxide and attributed to an NH signal. The presence of an NH signal suggests that one of the thiourea nitrogens is not coordinated. These data are consistent with square-pyramidal Re^VO complexes with N,S coordination of the thiourea, giving an N_2S_2 basal donor set.

^1H NMR spectra of **6b** recorded at 23 °C and −50 °C were similar, and only one set of the two doublets (6.94 and 7.31 ppm, J = 9 Hz) was observed in the aromatic region, suggesting that only one of two possible conformers was present. Fast interconversion between two conformers at room temperature should be slowed at −50 °C, and either signals for two species would be resolved or the broadening of signals would be observed. Furthermore, while one signal was observed for the two methyl groups in ligands **4e** and **5e**, two singlets (3.31 and 3.43 ppm) of equal intensity were observed for complex **6e**. This inequivalence of the methyl signals suggests that there is restricted rotation around $C-N(CH_3)_2$ bound and an extended π electron system in the thiourea moiety. Since the bidentate thiourea ligands represent a new class of chelating agents, the structure of **6a** was determined by X-ray diffraction methods.

X-ray Crystallography. In the solid state, two crystallographically independent molecules of **6a** were present. Final atomic coordinates are listed in Table 2, and perspective drawings of both molecules (A and B) are presented in Figure 1. Selected bond lengths and bond angles are given in Table 3. The coordination geometry of **6a** is typical of a $M^V{=}O(N_2S_2)$ (M = Re, Tc) complex.[20,28,30,31] The complex is five-coordinate with an N_2S_2 basal donor set and an apical oxo ligand; the metal atom is displaced 0.8 Å from the basal coordination plane toward the oxo ligand.

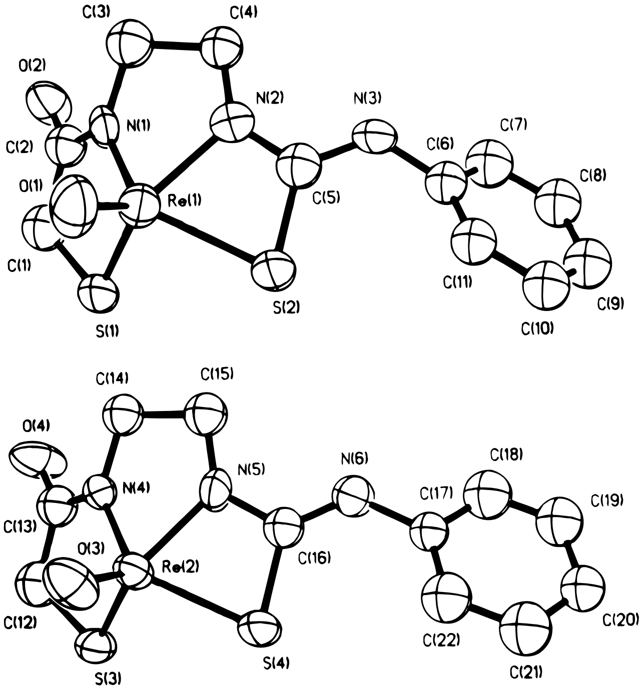

Figure 1. Perspective drawings of the two independent molecules A (top) and B (bottom) of [1-phenyl-3-(2-((2-thioacetyl)amino)ethyl)-thioureato]oxorhenium(V) (**6a**) with 50% probability for the thermal ellipsoids.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **6a**

Bond Lengths (Å)

Re(1)−O(1)	1.706(14)	Re(2)−O(3)	1.701(14)
Re(1)−N(1)	2.002(12)	Re(2)−N(4)	1.976(10)
Re(1)−N(2)	2.014(12)	Re(2)−N(5)	1.988(11)
Re(1)−S(1)	2.269(5)	Re(2)−S(3)	2.268(4)
Re(1)−S(2)	2.409(4)	Re(2)−S(4)	2.383(5)
S(1)−C(1)	1.86(2)	S(3)−C(12)	1.80(2)
S(2)−C(5)	1.74(2)	S(4)−C(16)	1.77(1)
N(2)−C(5)	1.30(2)	N(5)−C(16)	1.33(2)
N(2)−C(4)	1.46(2)	N(5)−C(15)	1.47(2)
N(3)−C(5)	1.36(2)	N(6)−C(16)	1.34(2)
N(3)−C(6)	1.41(2)	N(6)−C(17)	1.43(2)

Bond Angles (deg)

O(1)−Re(1)−N(1)	112.6(6)	O(3)−Re(2)−N(4)	113.2(6)
O(1)−Re(1)−N(2)	116.1(8)	O(3)−Re(2)−N(5)	115.8(6)
N(1)−Re(1)−N(2)	76.8(5)	N(4)−Re(2)−N(5)	76.5(4)
O(1)−Re(1)−S(1)	112.1(5)	O(3)−Re(2)−S(3)	109.7(4)
N(1)−Re(1)−S(1)	83.3(4)	N(4)−Re(2)−S(3)	83.4(4)
N(2)−Re(1)−S(1)	131.7(6)	N(5)−Re(2)−S(3)	134.3(5)
O(1)−Re(1)−S(2)	110.8(5)	O(3)−Re(2)−S(4)	111.4(5)
N(1)−Re(1)−S(2)	132.9(4)	N(4)−Re(2)−S(4)	131.9(4)
N(2)−Re(1)−S(2)	68.3(4)	N(5)−Re(2)−S(4)	68.6(3)
S(1)−Re(1)−S(2)	96.8(2)	S(3)−Re(2)−S(4)	97.9(2)
C(1)−S(1)−Re(1)	100.7(6)	C(12)−S(3)−Re(2)	100.1(6)
C(5)−S(2)−Re(1)	77.6(6)	C(16)−S(4)−Re(2)	79.3(6)
C(2)−N(1)−Re(1)	125.3(10)	C(13)−N(4)−Re(2)	123.9(9)
C(3)−N(1)−Re(1)	114.1(11)	C(14)−N(4)−Re(2)	115.9(9)
C(5)−N(2)−C(4)	129(2)	C(16)−N(5)−C(15)	125.5(13)
C(5)−N(2)−Re(1)	104.2(10)	C(16)−N(5)−Re(2)	106.6(9)
C(4)−N(2)−Re(1)	121.3(9)	C(15)−N(5)−Re(2)	123.0(9)
C(5)−N(3)−C(6)	126.6(12)	C(16)−N(6)−C(17)	127.9(12)
N(2)−C(5)−N(3)	123.4(14)	N(5)−C(16)−N(6)	126.0(13)
N(2)−C(5)−S(2)	109.8(12)	N(5)−C(16)−S(4)	105.5(11)
N(3)−C(5)−S(2)	126.2(13)	N(6)−C(16)−S(4)	127.9(13)

The $M-S-CH_2-C(O)-N$[20,28,32−35] and $M-N-CH_2-CH_2-N$[20,28,29] (M = Re, Tc) chelate rings are found in a number of

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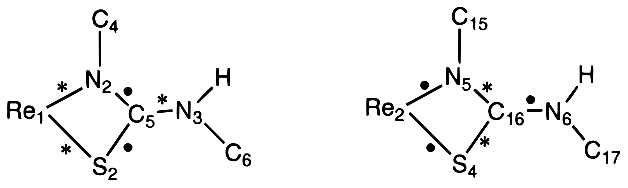
five-coordinate $M^{V}{=}O$ complexes with N and S donor atoms. Compared to those of these complexes, the analogous geometrical parameters of **6a** are generally not significantly different, suggesting that terminating a multidentate ligand with a thiourea function is compatible with chelate groups already in use. However, the values for **6a** often lie outside the ranges previously observed (Supporting Information). Since most of the surveyed complexes have terminating deprotonated thiol or deprotonated amide donor groups, the differences may be attributed in part to the introduction of a neutral S donor atom. Terminating neutral S donor atoms are found in both **6a** and ^{99}TcO(ema(morph)) (ema(morph) = trianionic form of *N*-[2-((2-(thioacetyl)amino)ethyl]-2-[(2-morpholinylthyl)thio]acetamide), and both complexes have short M−S(thiol) bond distances and small *trans*-S(thiol)−M−N bond angles[20] compared to the other complexes. However, for ^{99}TcO(ema(morph)), the geometrical parameters [other than the Tc−S(thiol) bond distance and *trans*-S(thiol)−Tc−N bond angle] are unremarkable. Therefore, the thiourea in **6a** probably has a slight but unique influence on the bonding of the other two chelate rings. This influence has extended the range observed for most of the geometrical parameters involving the M−S−CH_2−C(O)−N and M−N−CH_2−CH_2−N chelate rings in $MO(N_3S)$ and $MO(N_2S_2)$ complexes (Supporting Information).[20,28,32−35]

Although thiourea is a common ligand in transition metal chemistry, the bidentate coordination of the thiourea moiety in **6a** is quite rare. Normally thiourea coordinates through S in a monodentate manner.[6−9,36,37] Several $M^{V}{=}O$ (M = Re, Tc) complexes with monodentate thiourea ligands have been characterized with M−S(thiocarbonyl) bond distances ranging from 2.311(7) to 2.356(5) Å.[6,7,10,16] Compared to these M−S(thiocarbonyl) bond distances, those of **6a** are long (Table 3). In all but one comparison (Re−S(4) 2.356 (5) Å in **6a** and Re−S(2) 2.383 (5) Å in [ReO(H_2O)-*cis*-Cl_2-*cis*-$(tu)_2$]Cl),[6] the difference was significant. This result suggests that the Re−S(thiocarbonyl) bond distances in **6a** are influenced by chelation of the thiourea moiety, which results in a strained four-membered chelate ring. The N_c−C−S (N_c = coordinated N of thiourea) bond angles (109.8(12) and 105.5(11)°) in **6a** are significantly distorted from the 120° expected for sp^2-hybridized C. The N_u−C−S (N_u = uncoordinated N of thiourea) bond angles are >120° and are larger than the N_u−C−S bond angles in the monodentate thiourea ligands bound to Re(V) and Tc(V) (Supporting Information).[6,7,10,16]

A few examples of bidentate thiourea coordination have been confirmed by single-crystal X-ray diffraction studies and include Rh^{III}Cl(*N*,*N*-dimethylthiocarboxamido)(*N*,*N*-dimethyl-*N*′-phenylthioureato)(PPh_3),[14] Rh^{III}Cl(η-C_5Me_5){PhNC[N(C_6H_4Me-*p*)-CHNC_6H_4Me-*p*]S},[13] Cr^{III}(*N*,*N*′-diphenylthioureato)$_3$,[12] [Tc^{III}H-(tu)$(PMe_3)_4$][PF_6],[11] and Ni^{II}[(C_6H_5)NC(S)N{($C_2H_4)_2$O}]$_2$.[15] The N_c−C−S bond angles (109.4(4)−113(1)°) observed in these complexes are also significantly smaller than 120° and show that bidentate coordination of thiourea results in significant distortion of the ligand. However, the largest distortion was observed in molecule B of **6a**.

With the quadridentate TATU ligand, the narrowing of the N_c−C−S bond angle in **6a** allows for a Re−S(thiocarbonyl) bond distance that is normal compared to the Tc−S(thioether) bond distance in TcO(ema(morph)).[20] However, to compensate for the small four-membered chelate ring, both the S−Re−S (96.8(2) and 97.9(2)°) and C−N_c−C (129(2) and 125.5(13)°) bond angles are extended. In **6a,** these bond angles are significantly larger than those in known $MO(N_2S_2)$ complexes.[20,28,29]

Chart 1



molecule **A** molecule **B**

In both molecules the C−S(thiocarbonyl) and N_c−C(tu) bond distances (Table 3) within the thiourea are consistent with multiple-bond character and indicate that the metal is bound to an extended π system. The short N_u−C(tu) bond distances (Table 3) indicate that this π system extends beyond the metal coordination sphere. The presence of two methyl signals in the ^{1}H NMR spectrum of **6e** demonstrates restricted rotation about the C(tu)−N$(CH_3)_2$ bond consistent with this double-bond character. Because of the restricted rotation, two rotamers are possible with the monosubstituted derivatives. Only one rotamer was found in the solid state for **6a**, with the phenyl group *cis* to the thiocarbonyl. Also, for each of the monosubstituted derivatives (**6a**−**d**), only one set of NMR signals was observed; at low temperature, not even broadening was observed for **6b**. These results suggest that one rotamer is preferred and that, in both the solid and solution states, this preferred rotamer has the substituent *cis* to the thiocarbonyl.

The NMR results also show that rotation about the N_u−C(Ph) bond is rapid even at low temperature. Indeed, the N_u−C(Ph) bond distances are long compared to the N_u−C(tu) bond distances (Table 3), indicating that π overlap between the thiourea system and the aromatic system does not occur. This conclusion is supported by the tilting of the phenyl ring (42°, A; 26°, B) with respect to the metal-bound thiourea planes (Chart 1). The difference in the tilt angle results from the different lattice environments. Steric hindrance may be the cause of the positioning of the phenyl group *cis* to the thiocarbonyl. Indeed, this arrangement was also found in the Cr^{III}(*N*,*N*′-diphenylthioureato)$_3$ complex with bidentate thiourea coordination.[12]

The metal-bound thiourea moieties are nearly coplanar. The mean deviations from the best fit planes of the heavy atoms shown in Chart 1 are 0.121 Å (A) and 0.088 Å (B). The greater deviations for A than for B reflect the disruption of coplanarity between the best fit planes [N(2), C(5), S(2), N(3), H(N3), C(6)] (mean deviation 0.089 Å) and [Re(1), C(4), N(2), C(5) S(2), N(3)] (mean deviation 0.052 Å). The angle between these two planes is 10.0°.

Differences in the bond lengths and bond angles of the two molecules (A and B) were not significant. However, there were significant differences in some torsion angles (Table 4) reflecting, in particular, the difference in the positions of the phenyl rings (Figure 2). The torsion angle differences appear to be a result of a single H-bond between the two types of molecules in the crystal lattice; the uncoordinated N(3) atom of A was within H-bonding distance (2.810 Å) of the carbonyl O(4) atom of B (1.5 + *x*, 1 − *y*, 0.5 − *z*).

An interesting pattern in the bond distances was observed when molecule A was compared with molecule B (Chart 1):

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Table 4. Corresponding Torsion Angles (deg) for the Two Independent Molecules (A and B) in the Solid-State Structure of **6a** with Significant Differences[a]

A	angle	B	angle
N(1)−Re(1)−S(1)−C(1)	−14.12(0.76)	N(4)−Re(2)−S(3)−C(12)	−19.53(0.80)
S(2)−Re(1)−S(1)−C(1)	−146.71(0.65)	S(4)−Re(2)−S(3)−C(12)	−151.08(0.67)
S(2)−Re(1)−N(1)−C(2)	102.62(1.30)	S(4)−Re(2)−N(4)−C(13)	110.71(1.29)
C(2)−N(1)−C(3)−C(4)	−131.50(1.56)	C(13)−N(4)−C(14)−C(15)	−143.18(1.67)
C(6)−N(3)−C(5)−N(2)	−168.90(1.88)	C(17)−N(6)−C(16)−N(5)	172.14(1.61)
C(6)−N(3)−C(5)−S(2)	1.43(2.60)	C(17)−N(6)−C(16)−S(4)	−18.50(2.69)
C(5)−N(3)−C(6)−C(11)	−47.58(2.52)	C(16)−N(6)−C(17)−C(22)	−21.51(2.73)
C(5)−N(3)−C(6)−C(7)	137.96(1.76)	C(16)−N(6)−C(17)−C(18)	164.65(1.76)

[a] Number in parentheses represents the standard deviation.

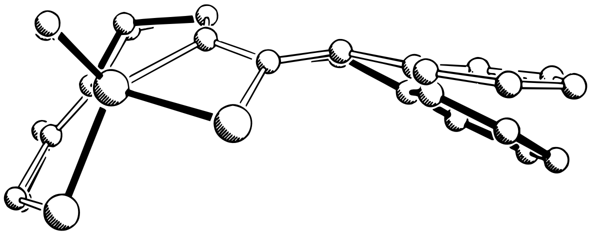

Figure 2. Best fit diagram (root-mean-square deviation 0.078 Å) of the heavy nonaromatic atoms in molecules A and B (**6a**).

longer bonds (compared with the sister molecule) are denoted by *; shorter bonds are denoted by •. The pattern may reflect a difference between A and B in the extended π system of the thiourea due to the H-bonding interaction. With the lack of coplanarity within the extended π system and short N_c−C(tu) and C−S(thiocarbonyl) bond distances in A, the thiourea becomes an inferior donor system, leading to longer metal−heteroatom bond distances.

Although interesting and believable, these trends in structural differences are small. It is clear that the four-membered ring will distort to allow fairly normal bonding distances between rhenium and the deprotonated thiourea moiety. Although this functionality may have small effects on the geometry of the other chelate rings and on the properties of the metal center, it is clear that the use of terminal thiourea functions is a new way to synthesize N_2S_2 type multidentate chelates.

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Supporting Information Available: Tables of crystal data and experimental parameters, atomic coordinates with equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, and H atom parameters as well as a view in *Pca*2_1 for **6a**, tables of analytical data for **4**−**6**, analytical, ^{1}H NMR and IR data for **2** and **4**−**6**, geometric parameters for complexes with M−S−$CH_2C(O)$−N and M−N−CH_2−CH_2−N chelate rings (M = Re, Tc), and geometric parameters for complexes with bidentate and monodentate thiourea ligands (13 pages). Ordering information is given on any current masthead page.

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