Synthesis, Characterization, and Protonation of an Amide-Containing Thiolate Complex of a Ruthenium Nitrosyl Porphyrin

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1-(Acetylamino)-2-methylpropane-2-thionitrite reacts with (OEP)Ru(CO) or $[(OEP)Ru]_2$ at room temperature to give the nitrosyl thiolate derivative, namely (OEP)Ru(NO)($SC(Me)_2CH_2NHC(O)Me$), in high yield. This nitrosyl thiolate complex is moderately air stable and has IR ν_{NO} and ν_{CO} bands at 1789 and 1673 cm^{-1}, respectively. Protonation of this complex with tetrafluoroboric acid and subsequent workup result in the formation of the *amide* complex, $[(OEP)Ru(NO)(O{=}C(Me)NHCH_2C(Me)_2SH)]BF_4$, in 92% yield. The crystal structures of the neutral (OEP)Ru(NO)($SC(Me)_2CH_2NHC(O)Me$) and cationic $[(OEP)Ru(NO)(O{=}C(Me)NHCH_2C(Me)_2SH)]BF_4$ complexes have been determined by single-crystal X-ray crystallography.

The biological roles of thionitrites (RSNO) continue to receive renewed attention[1−5] due to the observations that (i) nitrosation of the Cysβ93 residue in hemoglobin is reported to occur to give *S*-nitrosohemoglobin,[6] (ii) RSNO compounds can activate guanylyl cyclase in a manner independent of simple NO dissociation,[7−9] and (iii) trace metal ions catalyze RSNO decomposition.[10−12] These observations have raised the question of the possibility of a direct "ligand interaction" of RSNO with biologically important metal ions. Indeed, such a direct interaction between RSNO and the heme group in guanylyl cyclase was recently suggested as a possibility.[13]

Synthetic complexes of the form (por)M(NO)(SR) (por = porphyrinato dianion) are important as structural mimics for some biological systems. For example, cytochrome P450 contains a (por)Fe(SR) functionality that forms an adduct with NO to give the six-coordinate (por)Fe(NO)(SR) species in which the NO ligand is *trans* to the cysteinate group.[14−17] Nitric oxide synthase (NOS) also contains the (por)Fe(SR) functionality and binds NO to give a similar (por)Fe(NO)(SR) species,[18,19] although whether the latter process is physiologically relevant or not is still unclear. In any event, the (por)Fe(NO)(SR) derivatives are generally not very stable, and some biologically relevant (por)Fe(NO)(SR) complexes decompose via SR release to generate the stable five-coordinate (por)Fe(NO) species.[20] This observation led us to investigate synthetic ruthenium analogs of the form (por)Ru(NO)(SR) with the hope of obtaining thermally stable complexes.

We initially prepared air-stable and analytically pure (OEP)-Ru(NO)(SR) derivatives (OEP = octaethylporphyrinato dianion) via thiolate attack on the precursor ruthenium nitrosyl cation as shown in eq 1.[21] Bohle and co-workers also synthesized a

$$[(OEP)Ru(NO)(H_2O)]^+ + SR^- \rightarrow (OEP)Ru(NO)(SR) \quad (1)$$
$$R = CH_2CF_3\ (81\%),\ C_6F_4H\ (73\%)$$

$$(TTP)Ru(NO)(OMe) + p\text{-tolylSH} \rightarrow (TTP)Ru(NO)(S\text{-}p\text{-tolyl}) + MeOH \quad (2)$$

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Table 1. Crystal Data and Structure Refinement

	(OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me)	[(OEP)Ru(NO)(O=C(Me)NHCH$_2$C(Me)$_2$SH)]BF$_4$·CH$_2$Cl$_2$.0.5C$_6$H$_{14}$
empirical formula	$C_{42}H_{56}N_6O_2SRu$	$(C_{42}H_{57}N_6O_2SRu)(BF_4)(CH_2Cl_2)(0.5C_6H_{14})$
fw	810.06	1025.89
diffractometer	Siemens P4	Siemens P4/CCD
T, K	188(2)	133(2)
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimensions		
a, Å	10.465(2)) Å	13.7197(3)
b, Å	11.104(2)	14.0375(3)
c, Å	17.137(3)	14.3673(2)
α, deg	84.310(12)	89.367(2)
β, deg	78.28(2)	64.591(2)
γ, deg	79.902(11)	85.746(2)
V, Å^3; *Z*	1915.3(5); 2	2491.80(8); 2
D(calcd), g/cm^3	1.405	1.367
abs coeff, mm^{-1}	0.509	0.521
F(000)	852	1070
crystal size, mm	0.18 × 0.36 × 0.72	0.52 × 0.45 × 0.02
θ range for data collection, deg	1.87−25.00	2.72−29.34
index ranges	$0 \le h \le 12, -12 \le k \le 13, -19 \le l \le 20$	$-16 \le h \le 18, -18 \le k \le 19, 0 \le l \le 19$
no. of reflns collected	7150	25 972
no. of independent reflns	6747 [$R_{int} = 0.0585$]	11956 [$R_{int} = 0.0682$]
max and min transm	0.4389 and 0.3464	0.604 and 0.375
data/restraints/parameters	6727/0/487	11 956/0/580
goodness-of-fit on F^2	1.047	1.122
final *R* indices [$I > 2\sigma(I)$][a,b]	R1 = 0.0410, wR2 = 0.1021	R1 = 0.0933
R indices (all data)[a,b]	R1 = 0.0532, wR2 = 0.1142	R1 = 0.1495, wR2 = 0.2656
largest diff peak and hole, e Å^{-3}	0.917 and −0.908	2.311 and −1.576

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

related compound by a thiol exchange reaction of the precursor methoxide as shown in eq 2 (TTP = tetratolylporphyrinato dianion).[22]

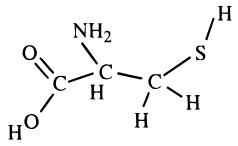
We also recently reported the synthesis of such ruthenium nitrosyl thiolates by an unusual *trans*-addition of thionitrites (eq 3),[23,24] a process that has since been successfully extended to osmium porphyrins (eqs 3 and 4).[25] The reaction of thionitrites

$$(por)M(CO) + RSNO \rightarrow (por)M(NO)(SR) \qquad (3)$$

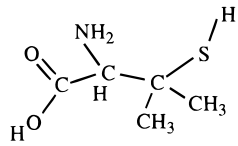
$$(por)M = (OEP)Ru, (OEP)Os, (TTP)Os$$

$$[(OEP)Os]_2 + 2RSNO \rightarrow 2(OEP)Os(NO)(SR) \qquad (4)$$

with *ferrous* (TPP)Fe(THF)$_2$ yields (TPP)Fe(NO) (TPP = tetraphenylporphyrinato dianion), whereas the related reaction with *ferric* [(TPP)Fe(THF)$_2$]$^+$ gives a mixture of the (TPP)Fe(NO) and [(TPP)Fe(NO)L]$^+$ nitrosylated products.[24] We proposed, on the basis of IR spectral data, that the formal *trans*-additions occurred via *S*-binding of the RSNO ligand to the metal centers. Notably, our thionitrite *trans*-additions to Ru porphyrins to date had only involved *primary* carbons (as in *N*-acetylcysteine methyl ester) attached to the sulfur atom of RSNO. Our related attempts at adding trityl thionitrite (Ph$_3$CSNO) have so far not been successful. We were thus interested in determining whether we could extend the addition reaction to alkanethiolates with *tertiary* carbon groups such as those that exist in penicillamine. In particular, we wanted to investigate whether the potential steric bulk at sulfur in *tertiary* *alkyl* thionitrites could then preclude such an addition to the metal center in a metalloporphyrin.



Cysteine



Penicillamine

In this paper, we demonstrate that the unusual *trans*-addition process also occurs for such a tertiary alkyl RSNO ligand. By choosing an amide-containing RSNO ligand that is soluble in organic solvents, we show that protonation of the resulting (OEP)Ru(NO)(SR) generates a novel cationic ruthenium amide adduct.

Experimental Section

All reactions were performed under an atmosphere of prepurified nitrogen using standard Schlenk glassware or in an Innovative Technology Labmaster 100 drybox. Solutions for spectral studies were also prepared under a nitrogen atmosphere. Solvents were distilled from appropriate drying agents under nitrogen just prior to use: CH_2Cl_2 (CaH_2), hexane (Na/benzophenone/tetraglyme).

Instrumentation. Infrared spectra were recorded on a Bio-Rad FT-155 FTIR spectrometer. ^{1}H NMR spectra were obtained on a Varian XL-300 spectrometer and the signals referenced to the residual signal of the solvent employed. All coupling constants are given in hertz. FAB mass spectra were obtained on a VG-ZAB-E mass spectrometer. UV−vis spectra were recorded on a Hewlett-Packard HP8453 diode array instrument.

Chemicals. (OEP)Ru(CO), HBF_4 (48 wt % solution in water), HBF_4 (54 wt % solution in Et_2O), and $NOBF_4$ were purchased from Aldrich Chemical Co. and used as received. 1-(Acetylamino)-2-methylpropane-2-thiol was prepared from the precursor 1-amino-2-methylpropane-2-thiol hydrochloride (97%, Aldrich) as described in the literature.[26] The thionitrite derivative MeC(O)NHCH$_2$C(Me)$_2$SNO was prepared from

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the precursor thiol with $NaNO_2$ in acid solution.[27] $[(OEP)Ru]_2$ was prepared by the literature method.[28] Chloroform-*d* (99.8%, Cambridge Isotope Laboratories) was vacuum-distilled from CaH_2 under nitrogen prior to use. Benzene-d_6 (99.6%, Cambridge Isotope Laboratories) was vacuum-distilled from Na under nitrogen prior to use. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Preparation of (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me). Method I. To a stirred CH_2Cl_2 solution (10 mL) of (OEP)Ru(CO) (0.050 g, 0.076 mmol) was added $MeC(O)NHCH_2C(Me)_2SNO$ (0.014 g, 0.079 mmol). The mixture was stirred for 10 min, during which it turned from red to dark purple. The solvent was removed in *vacuo*, the residue was dissolved in CH_2Cl_2/hexane (10 mL/5 mL), and crystals were obtained by slow evaporation of the solvent mixture in air to give $(OEP)Ru(NO)(SC(Me)_2CH_2NHC(O)Me)\cdot 0.25CH_2Cl_2$ (0.057 g, 0.069 mmol, 91% isolated yield). Anal. Calcd for $C_{42}H_{56}O_2N_6SRu\cdot 0.25CH_2Cl_2$: C, 61.04; H, 6.85; N, 10.11; Cl, 2.14; S, 3.86. Found: C, 61.47; H, 7.06; N, 10.05; Cl, 2.87; S, 3.59. IR (KBr, cm^{-1}): $\nu_{NO} = 1789$; $\nu_{CO} = 1673$; also 2964 m, 2932 w, 2869 w, 1513 m, 1504 m, 1464 m, 1446 m, 1360 w, 1318 w, 1273 m, 1227 w, 1151 m, 1111 w, 1055 m, 1020 m, 992 m, 962 m, 838 w, 745 w, 721 w, 546 w. ^{1}H NMR ($CDCl_3$): δ 10.30 (s, 4H, *meso*-H of OEP), 5.28 (s, 0.5H, CH_2Cl_2), 4.16 (m, 16H, CH_2CH_3 of OEP), 1.98 (t, $J = 7$, 24H, CH_2CH_3 of OEP), 1.42 (br, 1H, $C(CH_3)_2CH_2NHC(O)CH_3$), 1.22 (s, 3H, $C(CH_3)_2CH_2NHC(O)CH_3$), −0.87 (d, $J = 6$, 2H, $C(CH_3)_2CH_2NHC(O)CH_3$), −2.07 (s, 6H, $C(CH_3)_2CH_2NHC(O)CH_3$). Low-resolution mass spectrum (FAB): *m/z* 780 $[(OEP)Ru(SC(CH_3)_2CH_2NHC(O)CH_3)]^+$ (12%), 664 $[(OEP)Ru(NO)]^+$ (100%), 634 $[(OEP)Ru]^+$ (43%). UV-vis spectrum (λ, nm (ϵ, mM^{-1} cm^{-1}), 1.20×10^{-5} M in CH_2Cl_2): 347 sh (32), 393 (98), 407 sh (74), 546 (9), 572 (8).

Method II. To a C_6D_6 (0.5 mL) solution of $[(OEP)Ru]_2$ (0.005 g, 0.004 mmol) in an NMR tube was added $MeC(O)NHCH_2C(Me)_2SNO$ (0.0015 g, 0.0085 mmol). The ^{1}H NMR spectrum was collected after shaking the tube several times over a 10 min period to mix the reagents. Only the peaks of the nitrosyl thiolate product (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me) were observed in the NMR spectrum, indicating the quantitative nature of the reaction. ^{1}H NMR (C_6D_6): δ 10.48 (s, 4H, *meso*-H of OEP), 3.99 (q, $J = 7$, 16H, CH_2CH_3 of OEP), 1.90 (t, $J = 7$, 24H, CH_2CH_3 of OEP), 1.72 (br, 1H, $C(CH_3)_2CH_2NHC(O)CH_3$), 1.22 (s, 3H, $C(CH_3)_2CH_2NHC(O)CH_3$), −0.36 (d, $J = 6$, $C(CH_3)_2CH_2NHC(O)CH_3$), −1.86 (s, 6H, $C(CH_3)_2CH_2NHC(O)CH_3$). IR (KBr, cm^{-1}): $\nu_{NO} = 1789$; $\nu_{CO} = 1673$.

Preparation of [(OEP)Ru(NO)(O=C(Me)NHCH$_2$C(Me)$_2$SH)]BF$_4$. To a stirred CH_2Cl_2 solution (10 mL) of (OEP)Ru(CO) (0.050 g, 0.076 mmol) was added $NOBF_4$ (0.009 g, 0.077 mmol). The color of the reaction solution changed from reddish pink to brown red over a 1 h period, and an IR spectrum showed the replacement of the 1919 cm^{-1} band due to ν_{CO} of (OEP)Ru(CO) with a new band at 1879 cm^{-1} assigned to the ν_{NO} of $[(OEP)Ru(NO)]BF_4$. Solid $HSC(Me)_2CH_2NHC(O)Me$ was then added to the reaction solution, and the mixture was stirred for an additional 5 min. The solvent was removed in *vacuo*, and the residue was dissolved in CH_2Cl_2/hexane (15 mL, 2:1). Slow evaporation of the solvent mixture in air gave $[(OEP)Ru(NO)(O{=}C(Me)NHCH_2C(Me)_2SH)]BF_4\cdot H_2O$ (0.057 g, 0.066 mmol, 95% isolated yield). Anal. Calcd for $C_{42}H_{57}O_2N_6SRuBF_4\cdot H_2O$: C, 55.08; H, 6.49; N, 9.18; S, 3.50. Found: C, 55.33; H, 6.34; N, 9.28; S, 3.97. IR (KBr, cm^{-1}): $\nu_{NO} = 1856$; $\nu_{CO} = 1593$; also 2965 m, 2931 w, 2870 w, 1464 m, 1451 m, 1374 m, 1273 w, 1228 w, 1152 m, 1109 m, 1056 s, 1021 s, 994 m, 962 m, 844 w, 731 w, 710 w, 678 m, 520 w. A weak band at 2492 cm^{-1} (br) may be assigned to ν_{SH}. ^{1}H NMR ($CDCl_3$): δ 10.49 (s, 4H, *meso*-H of OEP), 5.60 (br, 1H, $C(CH_3)_2CH_2NHC(O)CH_3$), 4.21 (q, $J = 7$, 16H, CH_2CH_3 of OEP), 2.01 (t, $J = 7$, 24H, CH_2CH_3 of OEP), −0.09 (s, 1H, $HSC(CH_3)_2CH_2NHC(O)CH_3$), −0.58 (s, 6H, $C(CH_3)_2CH_2NHC(O)CH_3$), −0.63 (d, $J = 6$, 2H, $C(CH_3)_2CH_2NHC(O)CH_3$), −2.98 (s, 3H, $C(CH_3)_2CH_2NHC(O)CH_3$). Low-resolution mass spectrum (FAB): *m/z* 664 $[(OEP)Ru(NO)]^+$ (100%), 634 $[(OEP)Ru]^+$ (31%). UV−vis spectrum (λ, nm (ϵ, mM^{-1} cm^{-1}), 1.1×10^{-5} M in CH_2Cl_2): 347 sh (35), 391 (132), 540 (6), 573 (7).

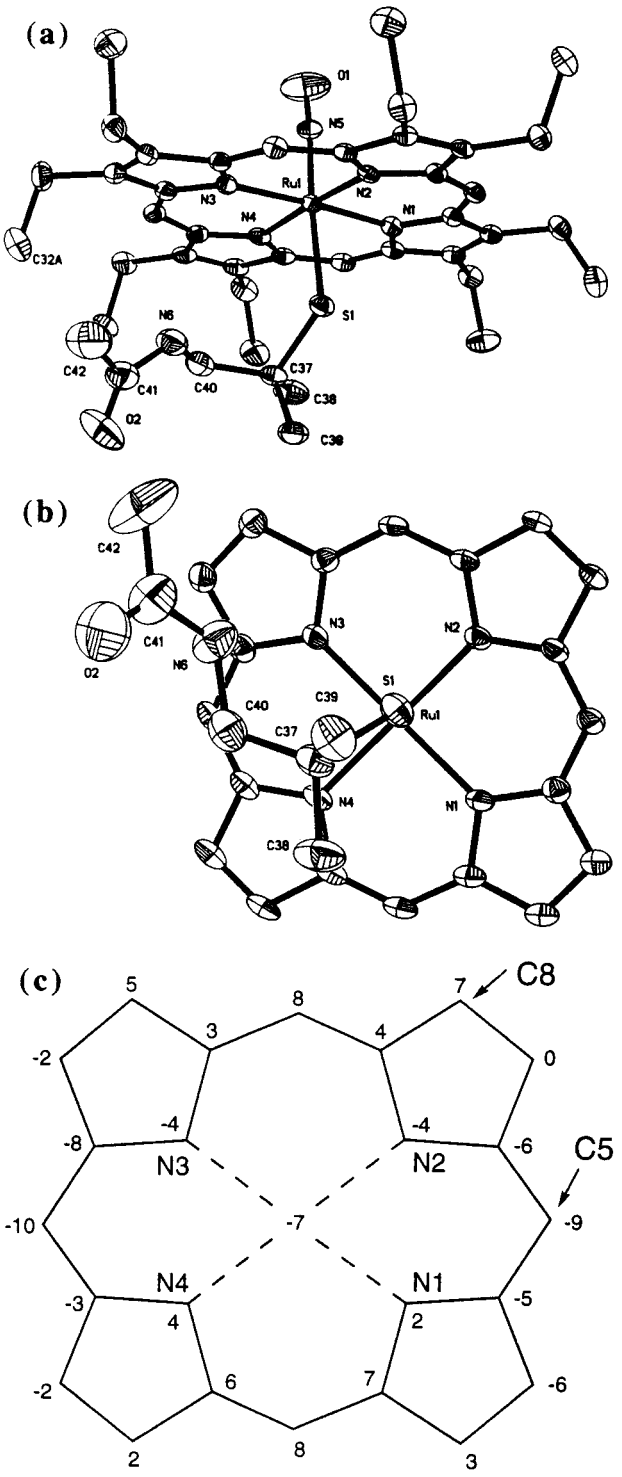

Figure 1. (a) Molecular structure of (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me). Hydrogen atoms have been omitted for clarity. (b) View of the thiolate orientation relative to the porphyrin core, with the view along the S-Ru bond. (c) Perpendicular atom displacements (in units of 0.01 Å) of the porphyrin core from the 24-atom mean porphyrin plane.

Protonation of (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me). Method I. To a $CDCl_3$ (1 mL) solution of (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me) (0.008 g, 0.001 mmol) was added 2 mL of aqueous HBF_4. The mixture was stirred vigorously for 10 min, and the $CDCl_3$ layer

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was separated from the water layer. The ^{1}H NMR spectrum of the $CDCl_3$ layer showed the formation of a mixture of [(OEP)Ru(NO)(O═C(Me)NHCH$_2$C(Me)$_2$SH)]BF_4 and the known [(OEP)Ru(NO)(H$_2$O)]BF_4 in a 10:87 ratio based on intergrations of the *meso*-H's of their OEP ligands.

Method II. To a CH_2Cl_2 (10 mL) solution of (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me) (0.050 g, 0.076 mmol) was added 6 μL of HBF_4·Et$_2$O (0.080 mmol). The mixture was stirred for 5 min, and the volatiles were removed in vacuo to give a residue whose IR spectrum (as a KBr pellet) was identical to that of authentic [(OEP)Ru(NO)(O═C(Me)NHCH$_2$C(Me)$_2$SH)]BF_4. The residue was dissolved in $CDCl_3$, and the ^{1}H NMR spectrum of this solution showed the formation of [(OEP)Ru(NO)(O═C(Me)NHCH$_2$C(Me)$_2$SH)]BF_4 in 92% yield.

Structural Determinations by X-ray Crystallography. Crystal data were collected using monochromated Mo Kα radiation (λ = 0.710 73 Å). Displacement ellipsoids in Figures 1 and 2 are drawn at the 50% probability level.

(i) (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me). A suitable crystal was grown from a CH_2Cl_2/hexane solution (5:1) left in air overnight. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scans was applied. The structure was solved by heavy-atom methods using the SHELXTL (Siemens) system and refined by full-matrix least-squares calculations based on F^2 using all reflections (SHELXL-93). Hydrogen atoms were included in the idealized positions. One of the ethyl carbon atoms (C(32)) was disordered at two sites and refined with 50% occupancy for each component (C(32A) and C(32B)). For 5722 "observed reflections" [$I > 2\sigma(I)$], the final R1 is 0.041. Details of the crystal data and refinement are given in Table 1 and in the Supporting Information.

(ii) [(OEP)Ru(NO)(HSC(Me)$_2$CH$_2$NHC(O)Me)]BF_4·CH_2Cl_2·0.5C_6H_{14}. A suitable crystal was grown as a thin plate from a CH_2Cl_2/hexane solution (3:1) left in the drybox overnight. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on equivalent data was applied. The structure was solved by direct methods and refined by full-matrix least-squares calcualtions based on on F^2 using all data (SHELXL-93). H atoms were included in the refinement. Most were initially located by idealized geometry—the hydrogens on N(6) and S(1) were located on a difference map. All hydrogens were refined with a riding model. For 7240 "observed data" [$I > 2\sigma(I)$], the final R1 is 0.093. The largest residual peaks in the final difference map are located about 1.0 Å from the Ru atom. Details of the crystal data and refinement are given in Table 1 and in the Supporting Information.

Results and Discussion

As stated in the introduction, we have previously shown that thionitrites with primary carbon atoms attached to sulfur add to (por)Ru(CO) compounds to give the nitrosyl thiolate derivatives (eq 3).[23,24]

Reaction of (OEP)Ru(CO) with 1 equiv of solid 1-(acetylamino)-2-methylpropane-2-thionitrite (a thionitrite containing a tertiary carbon attached to sulfur) generates, after workup, the elementally pure *trans*-addition product in 91% isolated yield (eq 5). This dark purple (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me) product is moderately air-stable in solution and can be stored in air in the solid state for at least 1 month without noticeable decomposition. It is recrystallized from CH_2Cl_2/hexane in air. It is readily soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$ and in aromatic solvents such as benzene and toluene. Its IR spectrum as a KBr pellet shows bands at 1789 and 1673 cm^{-1} assigned to ν_{NO} and ν_{CO}, respectively. The ν_{NO} band is similar to those of the three (OEP)Ru(NO)(SR) complexes reported to date (R = CH_2CF_3 (1782 cm^{-1}), C_6F_4H (1798 cm^{-1}), NACysMe (1791 cm^{-1})).[21,23,24] The ν_{CO} band of the coordinated thiolate is shifted by 21 cm^{-1} to higher wavenumbers relative to that of the precursor thionitrite (1652 cm^{-1}). The sharpness of the peaks in the ^{1}H NMR spectrum of (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me) is characteristic of the expected low-spin electron configuration of the Ru^{II} d^6 system (with the linear NO ligand formally considered as NO$^+$).[29] The ^{1}H NMR spectrum contains the characteristic OEP signals and shows that all the peaks due to the coordinated thiolate ligand are shifted upfield relative to those of the free thiol or thionitrite. For example, the ligand SC(C*H*$_3$)$_2$− and NC*H*$_2$C− peaks are shifted upfield by 3.26 and 4.09 ppm, respectively, from those of the free thiol. The amide N*H* and C(C*H*$_3$)═O peaks are also shifted upfield by 4.39 and 0.85 ppm, respectively, from those of the free thiol. Such upfield shifts are not unexpected due to coordination of organic *S*-donor groups to the (por)Ru fragment.[30] For example, the SC*H*$_3$ peak in the bis(thioether) (OEP)Ru(DecMS)$_2$ complex (DecMS = *n*-decyl methyl sulfide) appears upfield at −2.51 ppm in C_6D_6.[30] The mass spectrum of (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me) shows highest ion fragments due to loss of either the NO ligand (*m/z* 780) or the thiolate ligand (*m/z* 664).

Interestingly, the same nitrosyl thiolate product of eq 5 is also obtained in quantitative yield from the reaction of non-carbonyl-containing [(OEP)Ru]$_2$ dimer with the precursor thionitrite (eq 6), indicating that the presence of the carbonyl ligand (in eq 5) is not required for the formal *trans*-addition process to proceed.

$$[(OEP)Ru]_2 + 2RSNO \rightarrow 2(OEP)Ru(NO)(SR) \quad (6)$$

$$SR = SC(Me)_2CH_2NHC(O)Me$$

Prior to this study, only one X-ray structural determination of a (por)Ru(NO)(SR) complex had been reported in the

Table 2. Selected Bond Lengths and Angles for (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me)

Bond Lengths (Å)			
O(1)−N(5)	1.114(4)	Ru(1)−N(2)	2.057(2)
Ru(1)−N(5)	1.769(3)	Ru(1)−N(3)	2.060(3)
Ru(1)−S(1)	2.3901(10)	Ru(1)−N(4)	2.060(3)
S(1)−C(37)	1.852(3)	Ru(1)−N(1)	2.063(3)
O(2)−C(41)	1.183(6)	C(37)−C(38)	1.520(5)
N(6)−C(41)	1.341(5)	C(37)−C(39)	1.529(5)
N(6)−C(40)	1.438(5)	C(41)−C(42)	1.504(7)
C(37)−C(40)	1.530(5)		

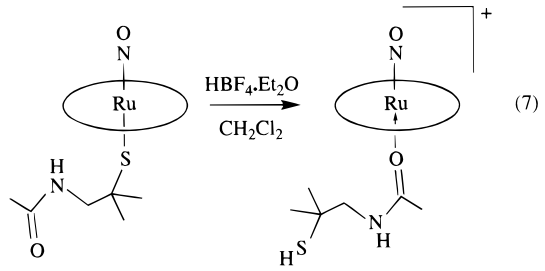
Bond Angles (deg)			
O(1)−N(5)−Ru(1)	172.8(3)	N(5)−Ru(1)−N(3)	92.54(12)
C(37)−S(1)−Ru(1)	121.74(13)	N(2)−Ru(1)−N(3)	90.40(10)
C(41)−N(6)−C(40)	123.7(4)	N(5)−Ru(1)−N(4)	88.16(12)
C(38)−C(37)−C(39)	109.5(3)	N(2)−Ru(1)−N(4)	176.15(10)
C(38)−C(37)−C(40)	108.3(3)	N(3)−Ru(1)−N(4)	89.51(11)
C(39)−C(37)−C(40)	109.8(3)	N(5)−Ru(1)−N(1)	90.77(12)
C(38)−C(37)−S(1)	111.8(3)	N(2)−Ru(1)−N(1)	89.66(10)
C(39)−C(37)−S(1)	103.9(2)	N(3)−Ru(1)−N(1)	176.66(10)
C(40)−C(37)−S(1)	113.5(2)	N(4)−Ru(1)−N(1)	90.20(10)
N(6)−C(40)−C(37)	114.7(3)	N(5)−Ru(1)−S(1)	175.32(9)
O(2)−C(41)−N(6)	123.7(5)	N(2)−Ru(1)−S(1)	79.68(7)
O(2)−C(41)−C(42)	119.9(5)	N(3)−Ru(1)−S(1)	88.19(8)
N(6)−C(41)−C(42)	116.4(4)	N(4)−Ru(1)−S(1)	96.47(8)
N(5)−Ru(1)−N(2)	95.69(12)	N(1)−Ru(1)−S(1)	88.53(8)

Table 3. Structurally Characterized Ruthenium Porphyrins with *S*-Donor Ligands

compound	metal oxidn state	Ru−N(por), Å	Ru−S, Å	Ru−S−C, deg	ref
(OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me)	II	2.063(3), 2.057(2) 2.060(3), 2.060(3)	2.3901(10)	121.74(13)	this work
(OEP)Ru(NO)(NACysMe-*S*)	II	2.057(5), 2.043(4) 2.045(6), 2.068(4)	2.362(2)	107.1(3)	23,24
(OEP)Ru(decMS)$_2$	II	2.044(3), 2.044(3) 2.056(3), 2.041(3)	2.376(1) 2.361(1)	107.5(1) 111.2(1) 109.0(1) 108.1(1)	30
(OEP)Ru(SPh$_2$)$_2$	II	2.050(3), 2.048(3)	2.371(1)	115.4(2) 110.9(2)	30
[(OEP)Ru(decMS)$_2$]BF$_4$	III	2.025(3), 2.047(3)	2.377(2)		46

literature, namely that of (OEP)Ru(NO)(NACysMe).[23,24] We were thus interested in obtaining the solid-state structure of (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me) to examine any structural changes due to the presence of the tertiary carbon attached to the sulfur center. The molecular structure is shown in Figure 1a, and the thiolate orientation and porphyrin atom displacements are shown in Figure 1b,c, respectively. Selected bond lengths and angles are listed in Table 2. The Ru−N(O) and N-O bond lengths are 1.769(3) and 1.114(3) Å, respectively, and the Ru−N-O bond is essentially linear with a bond angle of 172.8(3)°. The Ru−N(por) bond lengths average 2.060 Å, which is within the 2.03−2.068 Å range observed for other structurally characterized Ru^{II} porphyrins.[23,24,30−37] The porphyrin moiety exhibits a *ruffled* distortion.[38−43] The axial Ru−S distance is 2.3901(10) Å, which is longer that the Ru−S distances found in other structurally characterized ruthenium porphyrin thiolate or thioether complexes (Table 3) but is shorter than the Ru−S distance of 2.45 Å in *cis*,*cis*,*cis*-Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$.[44] The thiolate S−C(37) bond essentially eclipses a porphyrin nitrogen, with the N(4)−Ru−S−C(37) torsion angle of 10.4(2)° (Figure 1b). The thiolate Ru−S−C(37) angle is 121.74(13)°, and the corresponding S−C(37)−C(40) angle is 113.5(2)°. These angles are suggestive of an "opening up" of the thiolate ligand relative to the cysteinate ligand in (OEP)Ru(NO)(NACysMe),[23,24] where the corresponding angles are 107.1(3) (Ru−S−CH$_2$−) and 111.9(5)° (S−CH$_2$−C). The amide NH and C═O groups are in their usually favored *trans* arrangement,[45] and the S(1)−C(37)−C(40)−N(6) torsion angle is 52.3(4)°.

James and co-workers have shown that thioethers bind via their *S* atoms to the metal center in non-nitrosyl-containing Ru^{II} porphyrins.[30,46] We then proceeded to attempt to generate the coordinated *thiol* derivative via protonation of (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me). Protonation does indeed occur; however, we were intrigued to find out that the product obtained (92% yield) from the protonation with 1 equiv of HBF$_4$·Et$_2$O contained the *amide*-bound form of the thiol ligand (eq 7). We did not detect the presumed initial *S*-bound form of the ligand in the cationic product under our reaction conditions.



(7)

We have also obtained the same cationic [(OEP)Ru(NO)(O═C(Me)NHCH$_2$C(Me)$_2$SH)]BF$_4$ product in 95% isolated yield from the direct reaction of freshly prepared [(OEP)Ru(NO)]BF$_4$ (obtained by reacting (OEP)Ru(CO) with NOBF$_4$ in anhydrous CH$_2$Cl$_2$)[21] with 1 equiv of the organic amide-containing thiol.

The ν_{NO} of the cationic product (as a KBr pellet) is 67 cm^{-1} higher than that of the neutral precursor. The initial indication of the amide-binding formulation came from the shift in ν_{CO} of the coordinated ligand from 1673 cm^{-1} in the neutral ruthenium thiolate precursor to 1593 cm^{-1} in the cationic derivative, a shift of 80 cm^{-1}. The ν_{CO} of related unligated aldehydes and ketones seldom shift by more than 100 cm^{-1} to lower wavenumbers upon η^1-*O* coordination to metal centers.[47−50] Larger shifts (sometimes as high as 440 cm^{-1})[51] are obtained upon η^2-*C*,*O* coordination of aldehydes and ketones. The coordination chemistry of amides has been reviewed.[45] Importantly, com-

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plexation of a neutral amide group to a metal center also results in the lowering of the C═O bond order. The ^{1}H NMR spectrum in $CDCl_3$ reveals that whereas all the ligand peaks are shifted upfield from those of the free thiol, they are shifted downfield (with only one exception) from those of the coordinated thiolate in the precursor neutral complex. The exception is the C(CH_3)═O peak, which is now at −2.98 ppm, shifted by 4.2 ppm upfield from that of the thiolate complex (and −5.05 ppm from that of the free thiol). These data are consistent with a proposed amide-bound form of the thiol ligand in the cationic product complex in solution.

To unambiguously confirm the mode of attachment of the amide-containing thiol ligand in the protonated complex, we grew suitable crystals (as thin plates) for a single-crystal X-ray structural analysis. The structure of the cation is shown in Figure 2, which clearly demonstrates η^1-*O* binding of the amide-containing thiol ligand. Selected bond lengths and angles are listed in Table 4. The nitrosyl moiety is linear, with a Ru−N−O bond angle of 177.8(5)° and Ru−N(O) and N−O bond lengths of 1.708(6) and 1.141(7) Å, respectively. The Ru−N(por) bond length averages 2.050 Å, and the Ru atom is displaced by 0.10 Å from the 24-atom mean porphyrin plane toward the NO ligand. The porphyrin moiety exhibits a *saddle* distortion.[38−43] The axial Ru−O distance of 2.049(4) Å is shorter than other axial Ru−O distances (2.123−2.28 Å) in Ru^{II} porphyrins[31−37] but is longer than the Ru−O(alkoxide/alcohol) distances in (TPP)Ru^{III}(OEt)(EtOH) (2.019(3) Å),[52] [(TPP)-Ru^{IV}(*p*-$OC_6H_4Me)_2]_2O$ (1.944(11) Å),[52] and (TMP)Ru^{IV}-$(OCHMe_2)_2$ (1.892(3) Å; TMP = tetramesitylporphyrinato dianion).[53] The amide group is planar, and is oriented between a porphyrin nitrogen and a *meso*-carbon of the OEP macrocycle (Figure 2b), with the N(2)−Ru−O(2)−C(37) torsion angle of 28.7(7)°. Importantly, the amide C═O bond is lengthened (1.256(8) Å) compared to the amide C═O bond in the neutral ruthenium thiolate precursor (1.183(6) Å). Interestingly, the expected corresponding shortening of the amide (O═)C−N bond is not observed, but another structural factor needs to be considered also. The ligand N and S atoms are now effectively *trans* to each other with an N(6)−C(39)−C(40)−S(1) torsion angle of −175.0(5)°, implying that a net conformation change involving this four-atom fragment occurred during the protonation−isolation process of eq 7. The shortest distance from an F atom of the tetrafluoroborate anion to the cation is to the N(6) atom, with a distance of 2.888(7) Å and an idealized N(6)−H···F angle of 158°. These values are within those expected (2.5−3.2 Å, 130−180°) for moderate hydrogen bonds.[54]

Although dimethylformamide complexes of ruthenium porphyrins are known[35,55] and a few non-porphyrin ruthenium amide crystal structures have been reported,[56−59] to the best of our knowledge this is the first X-ray structural determination of a ruthenium porphyrin amide complex.

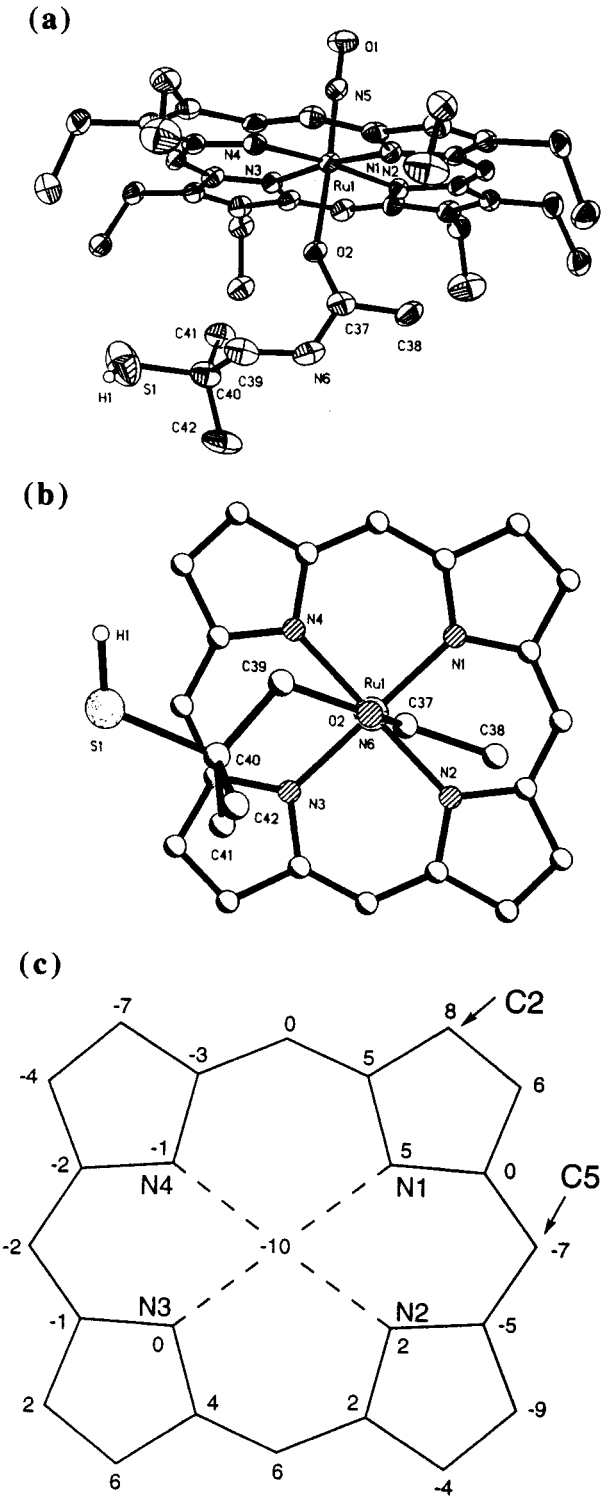

Figure 2. (a) Structure of the cation of [(OEP)Ru(NO)(O═C(Me)-$NHCH_2C(Me)_2SH$)]BF_4. (b) View of the amide orientation relative to the porphyrin core, with the view along the N6-O2-Ru atoms. (c) Perpendicular atom displacements (in units of 0.01 Å) of the porphyrin core from the 24-atom mean porphyrin plane.

Unlike the neutral precursor, the [(OEP)Ru(NO)(O═C(Me)-$NHCH_2C(Me)_2SH$)]BF_4 product is moisture sensitive in solution, the coordinated amide thiol of the complex in CH_2Cl_2 solution being displaced by a water ligand to give the known [(OEP)-Ru(NO)(H_2O)]BF_4 and free thiol over a 1 week period.

The presence of amide-binding of the thiol to the (OEP)Ru-

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Table 4. Selected Bond Lengths and Angles for [(OEP)Ru(NO)(O═C(Me)NHCH$_2$C(Me)$_2$SH)]BF$_4$

Bond Lengths (Å)			
O(1)−N(5)	1.141(7)	Ru(1)−N(2)	2.044(5)
Ru(1)−N(5)	1.708(6)	Ru(1)−N(3)	2.058(5)
Ru(1)−O(2)	2.049(4)	Ru(1)−N(4)	2.043(5)
S(1)−C(40)	1.821(9)	Ru(1)−N(1)	2.055(5)
O(2)−C(37)	1.256(8)	C(40)−C(41)	1.552(10)
N(6)−C(37)	1.314(9)	C(40)−C(42)	1.557(11)
N(6)−C(39)	1.444(10)	C(37)−C(38)	1.516(10)
C(39)−C(40)	1.526(10)		

Bond Angles (deg)			
O(1)−N(5)−Ru(1)	177.8(5)	N(5)−Ru(1)−N(3)	93.8(2)
C(37)−O(2)−Ru(1)	143.8(5)	N(2)−Ru(1)−N(3)	90.1(2)
C(37)−N(6)−C(39)	123.7(6)	N(5)−Ru(1)−N(4)	95.3(2)
C(41)−C(40)−C(42)	107.7(6)	N(2)−Ru(1)−N(4)	174.0(2)
C(41)−C(40)−C(39)	111.1(6)	N(3)−Ru(1)−N(4)	89.8(2)
C(42)−C(40)−C(39)	111.7(6)	N(5)−Ru(1)−N(1)	93.1(2)
C(41)−C(40)−S(1)	105.9(5)	N(2)−Ru(1)−N(1)	89.6(2)
C(42)−C(40)−S(1)	112.1(6)	N(3)−Ru(1)−N(1)	173.1(2)
C(39)−C(40)−S(1)	108.2(5)	N(4)−Ru(1)−N(1)	89.9(2)
N(6)−C(39)−C(40)	112.9(6)	N(5)−Ru(1)−O(2)	177.0(2)
O(2)−C(37)−N(6)	120.1(7)	N(2)−Ru(1)−O(2)	91.1(2)
O(2)−C(37)−C(38)	122.8(6)	N(3)−Ru(1)−O(2)	83.9(2)
N(6)−C(37)−C(38)	117.2(6)	N(4)−Ru(1)−O(2)	82.9(2)
N(5)−Ru(1)−N(2)	90.8(2)	N(1)−Ru(1)−O(2)	89.2(2)

(NO) fragment suggests that the thiol −SH group is perhaps not as good a binding group as the amide group in this complex. Indeed, the low propensity of the −SH group to bind to the (OEP)Ru(NO) fragment is further demonstrated by our observation (by ^{1}H NMR and IR spectroscopy) that protonation of the known (OEP)Ru(NO)(SCH$_2$CF$_3$) with triflic acid under anhydrous conditions generates the free thiol and (OEP)Ru(NO)(OTf). Indeed, when the protonation of the neutral (OEP)Ru(NO)(SC(Me)$_2$CH$_2$NHC(O)Me) precursor is performed with *aqueous* HBF$_4$, an 87:10 mixture of [(OEP)Ru(NO)(H$_2$O)]BF$_4$ and [(OEP)Ru(NO)(O═C(Me)NHCH$_2$C(Me)$_2$SH)]BF$_4$ is obtained. Needless to say, longer reaction times in the latter reaction favor the formation of [(OEP)Ru(NO)(H$_2$O)]BF$_4$.

We have shown that a tertiary alkyl thionitrite adds to a ruthenium porphyrin to give the nitrosyl thiolate *trans*-addition product. We have also demonstrated that the amide-containing thiolate ligand binds to the (OEP)Ru(NO) fragment via its sulfur atom. Interestingly, addition of a proton to this complex leads to a net rearrangement of the binding mode of the resulting thiol ligand to favor amide−binding of the ligand to the cationic [(OEP)Ru(NO)]$^+$ fragment. Further studies to investigate the mechanism of the protonation-rearrangement process are underway.

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Supporting Information Available: Labeled structural diagrams and listings of crystal data, structure refinement details, atomic coordinates, anisotropic displacement parameters, bond lengths and angles, hydrogen coordinates and isotropic displacement parameters, torsion angles, and least-squares planes (36 pages). Ordering information is given on any current masthead page.

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