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Synthesis and Characterization of Thiolate−Thiol Complexes of Ruthenium Nitrosyl Porphyrins and Their Symmetrical and Unsymmetrical Dithiolate-Bridged Bimetallic Derivatives

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Monometallic nitrosyl thiolate−thiol complexes of the form (por)Ru(NO)(S(CH_2)$_n$SH) (por = TPP, $n = 2$; TTP, $n = 2-4$) have been prepared in 49−61% isolated yields from the reaction of the (por)Ru(NO)(O-*i*-C_5H_{11}) alkoxide precursors with HS(CH_2)$_n$SH. The (OEP)Ru(NO)(SCH_2CH_2SH) complex was prepared in 71% isolated yield via addition of $HSCH_2CH_2SNO$ to (OEP)Ru(CO). These (por)Ru(NO)(S(CH_2)$_n$SH) complexes have been fully characterized by elemental analyses, infrared and ^{1}H NMR spectroscopy, and by mass spectrometry. The molecular structure of (OEP)Ru(NO)(SCH_2CH_2SH) has been determined by single-crystal X-ray crystallography. The Ru−N−O moiety is linear with a bond angle of 170.9(9)°. The symmetrical bimetallic [(por)Ru(NO)]$_2$(μ-S(CH_2)$_n$S-*S,S′*) complexes (por$_1$ = por$_2$; i.e., TPP/TPP, TTP/TTP, OEP/OEP) have also been prepared by variations of the procedures used in the preparation of their monometallic derivatives, and they have been fully characterized by elemental analyses, infrared and ^{1}H NMR spectroscopy, and by mass spectrometry. The novel unsymmetric [(TPP)Ru(NO)](μ-SCH_2CH_2S-*S,S′*)[Ru(NO)(OEP)] complex has also been obtained, and the experimental and simulated ^{1}H NMR spectrum of the protons of the μ-dithiolate bridge indicate that all four protons are inequivalent.

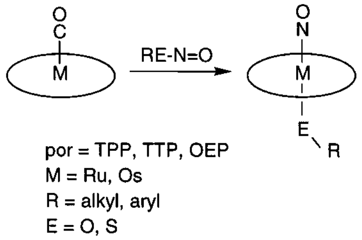
Introduction

The interest in the syntheses of compounds of the form (por)M(NO)(SR) (M = transition metal; por = porphyrinato dianion) stems from the fact that they are potential structural models for the NO adducts of the (por)Fe(SR) groups in cytochrome P450, chloroperoxidase and NO synthase.[1] We have reported the convenient syntheses of such (por)M(NO)(SR) compounds of Ru and Os by the unusual formal trans additions of thionitrites (RSNO) to the metalloporphyrin carbonyl and non-carbonyl precursors (e.g., Scheme 1).[2−4]

We have also investigated spectroscopic and structural relationships between these (por)M(NO)(SR) complexes and their alkoxide (por)M(NO)(OR) analogues (M = Ru, Os).[2,3] In investigating these (por)M(NO)(SR) complexes, we were interested in examining the potential synthetic utility of (por)M(NO)(S(CH_2)$_n$SH) complexes that contain a thiolate functionality (bound to the central metal) and a free thiol group. In particular, we were interested in preparing the hitherto unreported μ-dithiolate complexes of the form [(por)M]$_2$(μ-S(CH_2)$_n$S-*S,S′*). The lack of precedent of μ-dithiolate metalloporphyrins is somewhat surprising, given that related bimetallic porphyrin complexes containing bridging sulfido, alkyl, oxo, and related ligands are known.

The ethane-1,2-dithiolate (edt) ligand is known to exhibit diverse coordination chemistry.[5−8] Although numerous transition metal complexes containing chelating ethane-1,2-dithiolate and related ligands have been reported, surprisingly only a small handful of transition metal complexes containing *linear bridging* M(μ-S(CH_2)$_n$S-*S,S′*)M′ units have been synthesized. Examples of the latter binding modes with transition metals and other elements include those of Au,[9] Mo,[10] Zr,[11] Fe,[12] Rh,[13] Ti,[14] Sn,[15] and Sb.[16]

Scheme 1



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In this paper, we report our successful syntheses of bimetallic ruthenium porphyrin complexes containing μ-dithiolate ligands (edt = ethane-1,2-dithiolate; pdt = propane-1,3-dithiolate; btd = butane-1,4-dithiolate) using variations of the reactions described in Scheme 1. To the best of our knowledge, these are the first bimetallic porphyrin complexes containing μ-dithiolate ligands to be prepared for any metal.

Experimental Section

All reactions were performed under an atmosphere of prepurified nitrogen using standard Schlenk glassware and/or in an Innovative Technology Labmaster 100 Dry Box. 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), Et_2O (Na/benzophenone), hexane (Na/benzophenone/tetraglyme), benzene (Na).

Instrumentation. Infrared spectra were recorded on a Bio-Rad FT-155 FTIR spectrometer. Proton NMR spectra were obtained on Varian 400 or 300 MHz spectrometers and the signals referenced to the residual signal of the solvent employed. All coupling constants are in Hz. FAB mass spectra were obtained on a VG-ZAB-E mass spectrometer.

Chemicals. Compounds (por)Ru(CO) (por = TTP, TPP) were prepared by published procedures.[17] Isoamyl nitrite (97%), (OEP)Ru(CO), *t*-BuONO (96%), ethane-1,2-dithiol (edtH_2, $HSCH_2CH_2SH$, 90+%), propane-1,3-dithiol (pdtH_2, $HSCH_2CH_2CH_2SH$, 99%) and butane-1,4-dithiol (bdtH_2, $HSCH_2CH_2CH_2CH_2SH$, 97%) were purchased from Aldrich Chemical Co. and used as received. Chloroform-*d* (99.8%, Cambridge Isotope Laboratories) was vacuum-distilled from CaH_2 under nitrogen prior to use. Elemental analyses were performed by Atlantic Microlab (Norcross, GA).

Preparation of (TPP)Ru(NO)($OCH_2CH_2CHMe_2$). To a stirred CH_2Cl_2 solution (20 mL) of (TPP)Ru(CO) (0.200 g, 0.270 mmol) was added excess isoamyl nitrite (0.50 mL, 3.6 mmol). The mixture was stirred for 1 h during which time it turned from red to dark-purple. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and filtered through neutral alumina (2.5 × 20 cm). The volume of the filtrate was reduced to ca. 5 mL, and hexane (1 mL) was added. Crystals were obtained by slow evaporation of this mixture in air to give (TPP)Ru(NO)($OCH_2CH_2CHMe_2$)$\bullet$0.1CH_2Cl_2 (0.172 g, 0.205 mmol, 76% isolated yield). Anal. Calcd for $C_{49}H_{39}O_2N_5Ru\bullet0.1CH_2Cl_2$: C, 70.25; H, 4.71; N, 8.34. Found: C, 70.29; H, 4.95; N, 8.08. IR (CH_2Cl_2, cm^{-1}): ν_{NO} = 1809. IR (KBr, cm^{-1}): ν_{NO} = 1800 s; also 2952 w, 2866 w, 1596 m, 1529 w, 1486 m, 1441 m, 1351 m, 1307 m, 1209 m, 1176 m, 1119 w, 1071 s, 1015 s, 798 s, 753 s, 703 s, 665 m, 590 w, 529 m, 461 w. ^1H NMR ($CDCl_3$): δ 8.91 (s, 8H, *pyrrole*-H of TPP), 8.24 (m, 8H of TPP), 7.74 (m, 12H of TPP), 5.28 (s, 0.2H, C$H_2$$Cl_2$), −0.58 (d, *J* = 7, 6H, OCH_2CH_2CH*Me*$_2$), −1.03 (m, 1H, OCH_2CH_2C*H*Me_2), −2.36 (t, *J* = 7, 2H, OC*H*$_2CH_2CHMe_2$), −2.73 (apparent q (dt), *J* = 7/7, 2H, OCH_2C*H*$_2CHMe_2$). Low-resolution mass spectrum (FAB): *m*/*z* 744 [(TPP)Ru(NO)]$^+$ (100%), 714 [(TPP)Ru]$^+$ (41%).

Preparation of (OEP)Ru(NO)($OCH_2CH_2CHMe_2$). To a stirred CH_2Cl_2 solution (20 mL) of (OEP)Ru(CO) (0.150 g, 0.227 mmol) was added excess isoamyl nitrite (0.10 mL, 0.72 mmol). The mixture was stirred for 1 h during which time it turned from red to dark-purple (occasional vacuum was applied to the contents of the reaction flask for ca. 5 s every 15 min to remove excess NO gas generated by isoamyl nitrite decomposition). The solvent was then removed in vacuo. The crude product was dissolved in ether and filtered through neutral alumina in air. The volume of the filtrate was reduced in vacuo to ca. 5 mL, and hexane (1 mL) was added. Crystals were obtained by slow evaporation of this mixture in air to give (OEP)Ru(NO)($OCH_2CH_2CHMe_2$) (0.107 g, 0.142 mmol, 62% isolated yield). Anal. Calcd for $C_{41}H_{55}O_2N_5Ru$: C, 65.57; H, 7.38; N, 9.33. Found: C, 65.33; H, 7.48; N, 9.18. IR (CH_2Cl_2, cm^{-1}): ν_{NO} = 1800. IR (KBr, cm^{-1}): ν_{NO} = 1788 s; also 2964 m, 2932 m, 2869 m, 1466 m, 1449 m, 1371 w, 1316 w, 1272 w, 1228 vw, 1152 m, 1112 vw, 1058 m, 1019 m, 992 m, 961 m, 840 m, 746 m, 599 w. ^1H NMR ($CDCl_3$): δ 10.28 (s, 4H, *meso*-H of OEP), 4.15 (q, *J* = 8, 16H, C*H*$_2CH_3$ of OEP), 1.99 (t, *J* = 8, 24 H, CH_2C*H*$_3$ of OEP), −0.68 (d, *J* = 7, 6H, OCH_2CH_2CH*Me*$_2$), −1.19 (m, 1H, OCH_2CH_2C*H*Me_2), −2.82 (t, *J* = 7, 2H, OC*H*$_2CH_2CHMe_2$), −3.20 (apparent q (dt), *J* = 7/7, 2H, OCH_2C*H*$_2CHMe_2$). Low-resolution mass spectrum (FAB): *m*/*z* 664 [(OEP)Ru(NO)]$^+$ (100%), 634 [(OEP)Ru]$^+$ (70%).

Preparation of (TPP)Ru(NO)(SCH_2CH_2SH). To a stirred CH_2Cl_2 solution (20 mL) of (TPP)Ru(NO)($OCH_2CH_2CHMe_2$) (0.150 g, 0.180 mmol) was added ethane-1,2-dithiol (50 μL, 0.54 mmol). The color of the reaction solution changed from purple to green over a 10 min period. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (10 mL) and filtered through a silica gel column (160−200 mesh, 2.5 × 30 cm). A green band was collected, and the solvent was removed in vacuo to give (TPP)Ru(NO)(SCH_2CH_2SH) (0.085 g, 0.102 mmol, 57%) as a green powder. Anal. Calcd for $C_{46}H_{33}ON_5S_2Ru$: C, 66.01; H, 3.97; N, 8.37; S, 7.66. Found: C, 65.87; H, 4.06; N, 8.27; S, 7.77. IR (CH_2Cl_2, cm^{-1}): ν_{NO} = 1803. IR (KBr, cm^{-1}): ν_{NO} = 1792; also 3052 w, 3025 w, 1595 m, 1527 w, 1487 w, 1447 w, 1348 m, 1305 w, 1262 w, 1206 w, 1176 m, 1072 m, 1014 s, 796 m, 752 s, 704 s, 527 w. ^1H NMR ($CDCl_3$): δ 8.94 (s, 8H, *pyrrole*-H of TPP), 8.25 (m, 8H of TPP), 7.76 (m, 12H of TPP), −0.09 (t, *J* = 8, 1H, SCH_2CH_2S*H*), −0.78 (apparent q(dt), *J* = 8/ 8, 2H, SCH_2C*H*$_2SH$), −2.30 (t, *J* = 8, 2H, SC*H*$_2CH_2SH$). Low-resolution mass spectrum (FAB): *m*/*z* 744 [(TPP)Ru(NO)]$^+$ (100%), 714 [(TPP)Ru]$^+$ (58%).

Preparation of (TTP)Ru(NO)(SCH_2CH_2SH). To a stirred CH_2Cl_2 solution (10 mL) of (TTP)Ru(NO)($OCH_2CH_2CHMe_2$) (0.100 g, 0.113 mmol) was slowly added ethane-1,2-dithiol (11 μL, 0.12 mmol). The color of the reaction solution changed from dark-purple to green over a 1 h period. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2/hexane (1:1, 20 mL) and filtered through a silica gel column (2.5 × 20 cm). A green band was collected, and the solvent removed in vacuo to give (TTP)Ru(NO)(SCH_2CH_2SH) (0.062 g, 0.069 mmol, 61%) as a green powder. Anal. Calcd for $C_{50}H_{41}ON_5S_2Ru$: C, 67.24; H, 4.63; N, 7.84; S, 7.18. Found: C, 67.11; H, 4.70; N, 7.75; S, 7.30. IR (CH_2Cl_2, cm^{-1}): ν_{NO} = 1793. IR (KBr, cm^{-1}): ν_{NO} = 1770; also 3022 w, 2922 m, 2850 w, 1527 m, 1511 m, 1494 m, 1447 m, 1349 m, 1305 m, 1259 w, 1212 m, 1182 m, 1109 w, 1073 m, 1014 s, 846 m, 797 vs, 713 s, 521 s, 450 m. ^1H NMR ($CDCl_3$): δ 8.95 (s, 8H, *pyrrole*-H of TTP), 8.13 (t, *J* = 8, 8H of TTP), 7.55 (d, *J* = 8, 8H of TTP), 2.70 (s, 12H, C*H*$_3$ of TTP), −0.09 (t, *J* = 8, 1H, SCH_2CH_2S*H*), −0.82 (apparent q(dt), *J* = 8/8, 2H, SCH_2C*H*$_2SH$), −2.31 (t, *J* = 8, 1H, SC*H*$_2CH_2SH$). Low-resolution mass spectrum (FAB): *m*/*z* 800 [(TTP)Ru(NO)]$^+$ (100%), 770 [(TTP)Ru]$^+$ (68%).

Preparation of (OEP)Ru(NO)(SCH_2CH_2SH). To a stirred CH_2Cl_2 solution (20 mL) of (OEP)Ru(CO) (0.150 g, 0.227 mmol) was added a previously prepared red mixture (0.6 mL in 5 mL of CH_2Cl_2) of ethane-1,2-dithiol and isoamyl nitrite (1:2 ratio by volume, 1:1.3 mol ratio, 10 min mixing time). The color of the reaction solution changed from red purple to dark-purple over a 3 min period. The reaction was monitored by IR spectroscopy, and the reaction stopped when the ν_{CO} of the starting (OEP)Ru(CO) compound disappeared (ca. 10 min). The solvent was removed in vacuo, and the residue was dissolved in a Et_2O/CH_2Cl_2 (5:1, 10 mL) mixture and filtered through a neutral alumina column (2.5 × 20 cm) using Et_2O as added eluent. The purple filtrate was collected, and the solvent removed in vacuo to give (OEP)Ru(NO)(SCH_2CH_2SH)$\bullet$0.68CH_2Cl_2 (0.132 g, 0.162 mmol, 71%) as a purple powder. Anal. Calcd for $C_{38}H_{49}ON_5S_2Ru\bullet0.68CH_2Cl_2$: C, 57.01; H, 6.23; N, 8.59; S, 7.87; Cl, 5.92. Found: C, 57.53; H, 6.28; N, 8.34; S, 8.05; Cl, 6.34. IR (CH_2Cl_2, cm^{-1}): ν_{NO} = 1793. IR (KBr, cm^{-1}): ν_{NO} = 1779 s; also 2962 m, 2930 m, 2868 w, 1466 m, 1449 m, 1372 m, 1316 w, 1270 m, 1227 w, 1152 s, 1110 w, 1056 s, 1019 s, 992 s, 962 s, 841 m, 737 s, 714 m. ^1H NMR ($CDCl_3$): δ 10.29 (s, 4H, *meso*−H of OEP), 5.28 (s, C*H*$_2Cl_2$), 4.15 (m, 16H, C*H*$_2CH_3$ of OEP), 2.00 (t, *J* = 8, 24H, CH_2C*H*$_3$ of OEP), −0.31 (t, *J* = 8, 1H, SCH_2CH_2S*H*), −1.20 (m, 2H, SCH_2C*H*$_2SH$), −2.78 (m, 2H, SC*H*$_2CH_2SH$). Low-resolution mass spectrum (FAB): *m*/*z* 664 [(OEP)Ru(NO)]$^+$ (100%), 634 [(OEP)Ru]$^+$ (49%).

Preparation of [(TPP)Ru(NO)]$_2$(μ-edt-*S,S′*). To a CH_2Cl_2 (20 mL) solution of (TPP)Ru(NO)($OCH_2CH_2CHMe_2$) (0.075 g, 0.090 mmol) was added ethane-1,2-dithiol (9 μL, 0.1 mmol). The reaction mixture

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was stirred for 1 h, during which time the color changed from dark-purple to green. More (TPP)Ru(NO)($OCH_2CH_2CHMe_2$) (0.075 g, 0.090 mmol) was added, and the reaction mixture was stirred for a further 3 h. The solvent was removed in vacuo, and a ^{1}H NMR spectrum of the residue in $CDCl_3$ showed the presence of the desired bimetallic product and (TPP)Ru(NO)(SCH_2CH_2SH) in a 1:2 mole ratio, together with some unreacted (TPP)Ru(NO)($OCH_2CH_2CHMe_2$). The reaction mixture was stirred overnight. The solvent was removed in vacuo, and the residue was dissolved in a CH_2Cl_2/hexane (2:1) mixture and chromatographed through a silica gel column (2.5 × 30 cm). The first green band was collected, and the solvent removed in vacuo to give [(TPP)Ru(NO)]$_2$(μ-edt-*S,S′*) (0.032 g, 0.020 mmol, 22% (based on Ru)) as a green powder. Anal. Calcd for $C_{90}H_{60}O_2N_{10}S_2Ru_2$: C, 68.42; H, 3.83; N, 8.87; S, 4.06. Found: C, 68.27; H, 4.01; N, 8.61; S, 4.21. IR (CH_2Cl_2, cm^{-1}): $\nu_{NO} = 1802$. IR (KBr, cm^{-1}): $\nu_{NO} = 1779$ s; also 3052 vw, 3024 vw, 1596 m, 1528 w, 1486 m, 1440 m, 1349 m, 1306 m, 1260 w, 1208 w, 1175 m, 1071 s, 1014 s, 795 s, 751 s, 702 s, 666 w, 527 w. ^{1}H NMR ($CDCl_3$): δ 8.52 (s, 16H, *pyrrole*-H of TPP), 8.00 (d, $J = 7$, 8H of TPP), 7.68 (m, 20H of TPP), 7.44 (m, 12H of TPP), −5.73 (s, 4H, SCH_2CH_2S). Low-resolution mass spectrum (FAB): *m/z* 745 [(TPP)Ru(NO) + H]$^+$ (100%), 714 [(TPP)Ru]$^+$ (35%).

Leaving the reaction mixture to stir overnight (ca. 12 h total reaction time) resulted in an altered mole ratio (determined by ^{1}H NMR spectroscopy) of the desired bimetallic product, (TPP)Ru(NO)(SCH_2CH_2SH), and unreacted (TPP)Ru(NO)($OCH_2CH_2CHMe_2$) of 3:2:2; however, decomposition products began to form as well. In our experience, a 4−6 h reaction time maximized the formation of the desired bimetallic product in 34−40% isolated yields (based on Ru).

Preparation of [(TTP)Ru(NO)]$_2$(μ-edt-*S,S′*). This green product was prepared in a manner analogous to the TPP derivative described above. In our experience, a 4−6 h reaction time maximized the formation of the desired bimetallic product in 36−45% isolated yields (based on Ru). Anal. Calcd for $C_{98}H_{76}O_2N_{10}S_2Ru_2\cdot CH_2Cl_2$: C, 66.91; H, 4.42; N, 7.88; S, 3.61. Found: C, 66.85; H, 4.45; N, 7.97; S, 3.65. IR (CH_2Cl_2, cm^{-1}): $\nu_{NO} = 1788$. IR (KBr, cm^{-1}): $\nu_{NO} = 1770$ s; also 3022 w, 2918 w, 2865 w, 1527 m, 1511 m, 1494 m, 1446 m, 1349 m, 1304 m, 1268 w, 1212 m, 1182 m, 1108 w, 1073 m, 1014 s, 846 w, 797 vs, 712 s, 522 s, 450 w. ^{1}H NMR ($CDCl_3$): δ 8.53 (s, 16H, *pyrrole*-H of TTP), 7.88 (d, $J = 9$, 8H, *o*-H of TTP), 7.46 (d, $J = 7$, 8H, *o′*-H of TTP), 7.26 (m, 16H, *m*-H of TTP), 5.28 (s, CH_2Cl_2), 2.68 (s, 24H, *p*-CH_3 of TTP), −5.73 (s, 4H, SCH_2CH_2S). Low-resolution mass spectrum (FAB): *m/z* 1690 [[(TTP)Ru(NO)]$_2$(μ-SCH_2CH_2S)]$^+$ (0.2%), 800 [(TTP)Ru(NO)]$^+$ (100%), 770 [(TTP)Ru]$^+$ (41%).

Preparation of [(OEP)Ru(NO)]$_2$(μ-edt-*S,S′*). To a CH_2Cl_2 (20 mL) solution of (OEP)Ru(NO)(SCH_2CH_2SH) (0.040 g, 0.053 mmol) was added *t*-BuONO (0.10 mL, 0.81 mmol), and the mixture was stirred for 10 min. To the solution was added (OEP)Ru(CO) (0.035 g, 0.053 mmol), and the solution was stirred for a further 5 min, during which time the color changed from purple to red-purple. The solvent was removed in vacuo, the residue was dissolved in a benzene/hexane (5:1, 15 mL) mixture, and the solution chromatographed through a silica gel column (2.5 × 30 cm). The first dark-purple band was collected. Solvent removal in vacuo gave [(OEP)Ru(NO)]$_2$(μ-edt−*S,S′*)·0.2CH_2Cl_2 (0.027 g, 0.019 mmol, 36% (based on Ru)) as a purple powder. Anal. Calcd for $C_{74}H_{92}O_2N_{10}S_2Ru_2\cdot 0.2CH_2Cl_2$: C, 62.02; H, 6.48; N, 9.75; S, 4.46: Cl, 0.99. Found: C, 62.14; H, 6.64; N, 9.51; S, 4.43: Cl, 0.75. IR (CH_2Cl_2, cm^{-1}): $\nu_{NO} = 1786$. IR (KBr, cm^{-1}): $\nu_{NO} = 1770$ s; also 2964 m, 2930 m, 2869 w, 1466 m, 1448 m, 1375 m, 1316 w, 1271 m, 1226 w, 1176 vw, 1151 s, 1110 m, 1057 m, 1019 s, 992 m, 961 m, 838 m, 742 m, 710 m, 524 w. ^{1}H NMR ($CDCl_3$): δ 9.66 (s, 8H, *meso*-H of OEP), 3.79 (m, 32H, CH_2CH_3 of OEP), 1.65 (t, $J = 8$, 48H, CH_2CH_3 of OEP), −6.20 (s, 4H, SCH_2CH_2S). Low-resolution mass spectrum (FAB): *m/z* 664 [(OEP)Ru(NO)]$^+$ (100%), 634 [(OEP)Ru]$^+$ (27%).

Preparation of [(TPP)Ru(NO)](μ-edt-*S,S′*)[Ru(NO)(OEP)]. To a CH_2Cl_2 (20 mL) solution of (TPP)Ru(NO)(SCH_2CH_2SH) (0.050 g, 0.060 mmol) was added *t*-BuONO (50 μL, 0.40 mmol) for 10 min. To this solution was added (OEP)Ru(CO) (0.050 g, 0.075 mmol), and the solution was stirred for a further 10 min, during which time the color changed from green to brown-purple. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2/hexane (1:1, 15 mL) and filtered through a basic alumina column (2.5 × 30 cm). After removal of solvent, a 20:5:1 mixture of [(TPP)Ru(NO)](μ-edt-*S,S′*)[Ru(NO)(OEP)], [(TPP)Ru(NO)]$_2$(μ-edt-*S,S′*), and [(OEP)Ru(NO)]$_2$(μ-edt-*S,S′*) was obtained (0.022 g, ca. 24% combined yield). This solid mixture of the three bimetallic compounds was dissolved in CH_2Cl_2/hexane (1:1, 10 mL), and the solution was chromatographed through a second basic alumina column (2.5 × 40 cm). A red band eluted first, overlapping with a second brown band. This second brown band was collected, which consisted only of [(TPP)Ru(NO)](μ-edt-*S,S′*)[Ru(NO)(OEP)] and [(TPP)Ru(NO)]$_2$(μ-edt-*S,S′*). After redissolving the mixture (obtained from the second band) in CH_2Cl_2/hexane (1:2, 10 mL), the solution was chromatographed through a basic alumina column (2.5 × 40 cm). The first portion of a red-brown band was collected to give a small amount of [(OEP)Ru(NO)]$_2$(μ-edt-*S,S′*) and some [(TPP)Ru(NO)](μ-edt-*S,S′*)[Ru(NO)(OEP)]. The second (major) portion of this brown band was also collected to give spectroscopically pure [(TPP)Ru(NO)](μ-edt-*S,S′*)[Ru(NO)(OEP)]·0.3CH_2Cl_2 (0.005 g, 0.003 mmol, 5% yield (based on Ru)). Anal. Calcd for $C_{82}H_{76}O_2N_{10}S_2Ru_2\cdot 0.3CH_2Cl_2$: C, 64.80; H, 5.06; N, 9.18. Found: C, 64.99; H, 5.69; N, 8.77. IR (CH_2Cl_2, cm^{-1}): $\nu_{NO} = 1786$. IR (KBr, cm^{-1}): $\nu_{NO} = 1770$; also 2964 m, 2930 w, 2868 w, 1594 w, 1521 w, 1490 w, 1468 w, 1455 w, 1372 w, 1307 w, 1271 w, 1176 w, 1150 w, 1066 w, 1016 s, 996 m, 994 w, 908 w, 838 w, 796 w, 750 m, 733 m, 703 m. ^{1}H NMR ($CDCl_3$): δ 9.74 (s, 4H, *meso*-H of OEP), δ 8.46 (s, 8H, *pyrrole*-H of TPP), 7.96 (d, 4H, $J = 8$, Ph of TPP), 7.74 (m, 8H, Ph of TPP), 7.62 (m, 8H, Ph of TPP), 5.28 (s, CH_2Cl_2), 3.82 (m, 16H, CH_2CH_3 of OEP), 1.68 (t, 24H, CH_2CH_3 of OEP), −5.87 (app m (see text), 2H, SCH_2CH_2S), −5.97 (app m (see text), 2H, SCH_2CH_2S).

Protonation of [(OEP)Ru(NO)]$_2$(μ-edt-*S,S′*). To a $CDCl_3$ (1 mL) solution of [(OEP)Ru(NO)]$_2$(μ-edt-*S,S′*) (0.016 g, 0.011 mmol) was added $HBF_4\cdot Et_2O$ (2 μL, 0.03 mmol). The mixture was stirred for 10 min and then transferred to an NMR tube. The ^{1}H NMR spectrum of this solution revealed the formation of the previously reported [(OEP)Ru(NO)(H_2O)]BF_4 (≥95% yield by ^{1}H NMR) and free $HSCH_2CH_2SH$.

Preparation of (TTP)Ru(NO)($SCH_2CH_2CH_2SH$). To a stirred CH_2Cl_2 solution (20 mL) of (TTP)Ru(NO)($OCH_2CH_2CH(CH_3)_2$) (0.100 g, 0.113 mmol) was added propane-1,3-dithiol (50 μL, 0.49 mmol). The color of the reaction solution changed from dark-purple to green over a 1 h period. The solvent was removed in vacuo, and the crude product was dissolved in CH_2Cl_2/hexane (1/1) and filtered through a silica gel column (2.5 × 30 cm). A green band was collected. Solvent removal from the resulting green solution gave (TTP)Ru(NO)($SCH_2CH_2CH_2SH$)·0.4pdtH_2·0.3CH_2Cl_2·0.4hexane (0.056 g, 0.055 mmol, 49%) as a green powder. Anal. Calcd for $C_{51}H_{43}ON_5S_2Ru\cdot 0.4pdtH_2\cdot 0.3CH_2Cl_2\cdot 0.4$hexane: C, 65.26; H, 5.23; N, 6.93; S, 8.89; Cl, 2.11. Found: C, 66.52; H, 4.90; N, 7.24; S, 9.24; Cl, 2.46. IR(CH_2Cl_2, cm^{-1}): $\nu_{NO} = 1799$. IR (KBr, cm^{-1}): $\nu_{NO} = 1779$; also 3019 w, 2919 m, 2863 w, 1526 w, 1511 w, 1493 w, 1436 w, 1349 m, 1304 m, 1259 w, 1212 m, 1181 m, 1108 w, 1072 m, 1014 s, 846 w, 797 s, 714 m, 523 m. ^{1}H NMR ($CDCl_3$): δ 8.93 (s, 8H, *pyrrole*−H of TTP), 8.12 (d, $J = 8$, 8H of TTP), 7.55 (d, $J = 8$, 8H of TTP), 5.28 (s, 0.6H, CH_2Cl_2), 2.70 (s, 12H, *p*-CH_3 of TTP), 2.63 (pdtH_2), 1.88 (pdtH_2), 1.31 (pdtH_2), 1.27 (br, hexane), 0.88 (t, hexane), 0.54 (apparent q(dt), $J = 7/8$, 2H, $SCH_2CH_2CH_2SH$), −0.09 (t, $J = 8$, 1H, $SCH_2CH_2CH_2SH$), −1.07 (apparent quintet, $J = 7$, 2H, $SCH_2CH_2CH_2SH$), −2.55 (t, $J = 7$, 2H, $SCH_2CH_2CH_2SH$). Low-resolution mass spectrum (FAB): *m/z* 800 [(TTP)Ru(NO)]$^+$ (100%), 770 [(TTP)Ru]$^+$ (97%).

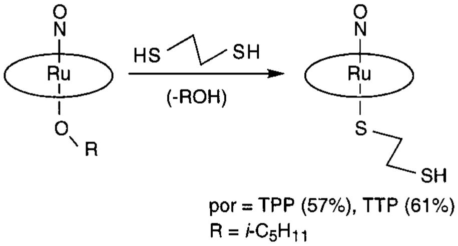
Preparation of [(TTP)Ru(NO)]$_2$(μ-pdt-*S,S′*). To a CH_2Cl_2 (20 mL) solution of (TTP)Ru(NO)($OCH_2CH_2CHMe_2$) (0.50 g, 0.056 mmol) was added propane-1,3-dithiol (6 μL, 0.06 mmol) and the mixture stirred for 1 h, during which time the color changed from dark-purple to green. To this solution was added more (TTP)Ru(NO)($OCH_2CH_2CHMe_2$) (0.500 g, 0.056 mmol), and the solution was stirred for 3 h, during which time the color changed from green to red-green. The solvent was removed in vacuo, and a ^{1}H NMR spectrum of the residue in $CDCl_3$ showed the presence of the desired but unstable bimetallic product and unreacted (TTP)Ru(NO)($OCH_2CH_2CHMe_2$) in a 4:1 mole ratio, together with an as-yet unidentified decomposition product (ca. 30%). The residue was dissolved in CH_2Cl_2/hexane (2/1) and chromatographed through a silica gel column (2.5 × 20 cm). The first green band was collected, and $[(TTP)Ru(NO)]_2(\mu\text{-pdt-}S,S')\cdot 0.2CH_2Cl_2$ (0.015 g, 0.009 mmol, 16% (based on Ru)) was isolated as a green powder by solvent removal. Anal. Calcd for $C_{99}H_{78}O_2N_{10}S_2Ru_2\cdot 0.2CH_2Cl_2$: C, 69.15; H, 4.59; N, 8.13. Found: C, 69.26; H, 4.82; N, 7.73. IR(CH_2Cl_2, cm^{-1}): ν_{NO} = 1790. IR (KBr, cm^{-1}): ν_{NO} = 1772; also 3021 w, 2922 w, 1560 vw, 1526 w, 1510 m, 1495 m, 1445 m, 1350 m, 1305 w, 1213 w, 1182 m, 1108 w, 1073 m, 1015 s, 797 s, 714 m, 523 s. ^{1}H NMR ($CDCl_3$): δ 8.63 (s, 16H, *pyrrole*-H of TTP), 7.93 (d, J = 8, 8H of TTP), 7.53 (d, J = 8, 8H of TTP), 7.47 (d, J = 8, 8H of TTP), 7.28 (d, J = 8, 8H of TTP), 5.28 (s, 0.4H, CH_2Cl_2), 2.68 (s, 24H, $p\text{-}CH_3$ of TTP), −4.18 (t, 4H, J = 8, $SC\mathit{H}_2CH_2C\mathit{H}_2S$), −4.64 (app m, 2H, $SCH_2C\mathit{H}_2CH_2S$). Low-resolution mass spectrum (FAB): m/z 800 $[(TTP)Ru(NO)]^+$ (100%), 770 $[(TTP)Ru]^+$ (84%).

Preparation of $(TTP)Ru(NO)(SCH_2CH_2CH_2CH_2SH)$. To a stirred CH_2Cl_2 solution (20 mL) of $(TTP)Ru(NO)(OCH_2CH_2CHMe_2)$ (0.150 g, 0.169 mmol) was added butane-1,4-dithiol (50 μL, 0.41 mmol). The color of the reaction solution changed from dark-purple to green over a 1 h period. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2/hexane (2/1) solvent and filtered through a silica gel column (2.5 × 30 cm). A green band was collected. The solvent was removed from this green band, and $(TTP)Ru(NO)(SCH_2CH_2CH_2CH_2SH)\cdot 0.2bdtH_2$ (0.093 g, 0.098 mmol, 58%) was isolated as a green powder. Anal. Calcd for $C_{52}H_{45}ON_5S_2Ru\cdot 0.2bdtH_2$: C, 67.06; H, 5.01; N, 7.41; S, 8.14. Found: C, 67.21; H, 5.47; N, 7.17; S, 8.10. IR (CH_2Cl_2, cm^{-1}): ν_{NO} = 1794. IR (KBr, cm^{-1}): ν_{NO} = 1770; also 3024 w, 2921 m, 2851w, 1566 m, 1554 m, 1529 w, 1513 w, 1444 w, 1384 w, 1349 m, 1303 w, 1265 w, 1211 w, 1181 m, 1107 w, 1072 m, 1014 s, 797 vs, 714 s, 523 m. ^{1}H NMR ($CDCl_3$): δ 8.92 (s, 8H, *pyrrole*−H of TTP), 8.10 (d, J = 8, 8H of TTP), 7.55 (d, J = 8, 8H of TTP), 2.70 (s, 12H, $C\mathit{H_3}$ of TTP), 2.50 ($bdtH_2$), 1.70 ($bdtH_2$), 1.33 ($bdtH_2$), 1.27 (m, 2H, $SCH_2CH_2CH_2C\mathit{H}_2SH$), 0.62 (t, J = 8, 1H, $SCH_2CH_2CH_2CH_2S\mathit{H}$), −0.26 (m, 2H, $SCH_2CH_2C\mathit{H}_2CH_2SH$), −1.35 (m, 2H, $SCH_2C\mathit{H}_2CH_2CH_2SH$), −2.65 (t, J = 8, 2H, $SC\mathit{H}_2CH_2CH_2CH_2SH$). Low-resolution mass spectrum (FAB): m/z 800 $[(TTP)Ru(NO)]^+$ (100%), 770 $[(TTP)Ru]^+$ (61%).

Attempted Preparation of $[(TTP)Ru(NO)]_2(\mu\text{-bdt-}S,S')$. To a CH_2Cl_2 (30 mL) solution of $(TTP)Ru(NO)(OCH_2CH_2CHMe_2)$ (0.100 g, 0.113 mmol) was added butane-1,4-dithiol (14 μL, 0.12 mmol) and the mixture stirred for 1 h, during which time the color changed from dark-purple to green. To this solution was added more $(TTP)Ru(NO)(OCH_2CH_2CHMe_2)$ (0.100 g, 0.113 mmol) and the solution was stirred for an additional 3 h, during which time the color changed from green to red-green. Chromatography of the resulting product(s) through a silica gel column gave a 5:1 mole ratio (by ^{1}H NMR spectroscopy) of $[(TTP)Ru(NO)]_2(\mu\text{-bdt-}S,S')$ and $(TTP)Ru(NO)(SCH_2CH_2CH_2CH_2SH)$, and a small amount (ca. 10%) of a third product which appears to arise from the decomposition of the bimetallic product. Attempts to obtain spectroscopically pure $[(TTP)Ru(NO)]_2(\mu\text{-bdt-}S,S')$ were unsuccessful, since it is very unstable in solution and decomposes to this as-yet unidentified product. ^{1}H NMR ($CDCl_3$) of $[(TTP)Ru(NO)]_2(\mu\text{-bdt-}S,S')$: δ 8.68 (s, 16H, *pyrrole*-H of TTP), 7.96 (d, J = 8, 8H of TTP), 7.67 (d, J = 8, 8H of TTP), 7.47 (d, J = 8, 8H of TTP), 7.29 (d, J = 8, 8H of TTP), 2.66 (s, 24H, $p\text{-}CH_3$ of TTP), −3.11 (br, 4H, $SCH_2C\mathit{H}_2C\mathit{H}_2CH_2S$), −3.71 (br, 4H, $SC\mathit{H}_2CH_2CH_2C\mathit{H}_2S$).

X-ray Structural Determination. A suitable crystal of $(OEP)Ru(NO)(SCH_2CH_2SH)\cdot CH_2Cl_2$ was grown from a CH_2Cl_2/hexane mixture by slow evaporation of the solvent in a Dry Box. The data were collected at −140 °C on a Siemens P4 diffractometer using Mo Kα (λ = 0.71073 Å) radiation. 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 the heavy atom method using the SHELXTL (Siemens) system and refined by full-matrix least-squares on F^2 using all reflections.

Scheme 2



The molecule has a crystallographically imposed center of symmetry and as a consequence the Ru atom should lie at the center of symmetry, and the axial nitrosyl and thiolate−thiol ligands should be completely disordered at two sites. However, better refinement was obtained in which the Ru atom is allowed to be disordered and moved 0.12 Å toward the axial NO group. Initially, the Ru atom was refined at the center of symmetry and gave elongated thermal ellipsoids (perpendicular to the porphyrin plane) and a very long Ru−N3 distance of 1.881(9) Å. In view of the fact that it is not uncommon for the NO ligand to cause slight vertical displacements of metal atoms in its metalloporphyrin complexes (see text), the structure was refined again in which the Ru atom was also allowed to refine as a disordered atom. The final refinement yielded much improved Ru−N(NO) and Ru−S bond lengths.

In addition to the Ru, NO and thiolate−thiol disorder, one of the carbon atoms of the ethyl groups of the porphyrin (C18) is also disordered at two sites. There is also a partially occupied site of a CH_2Cl_2 molecule which is highly disordered as indicated by the high thermal motions of its atoms (this CH_2Cl_2 molecule lies on the side of the porphyrin containing the NO ligand, where there are no close contacts with the NO group: C21···O1 = 3.33(2) Å). The asymmetric unit contains only half the molecule and half the CH_2Cl_2 molecule (50% occupancy was assumed for the CH_2Cl_2 atoms C21, Cl1, and Cl2 during refinement). Because of the disorder problem, considerable difficulty was encountered during the refinement of this structure. Several restraints were needed for stabilizing the refinement. The thermal parameter restraint (ISOR) was applied to the Ru1, N3, and C18A atoms, and the bond distance restraint (DFIX and SADI) were needed to restrain the axial NO and thiolate−thiol groups and the CH_2CH_2 bond lengths to chemically reasonable values. Because of the application of bond length restraints, any comparison or discussion of the axial group lengths should be done with caution. Hydrogen atoms were included in the refinement with idealized parameters, except the hydrogen atom on the terminal sulfur atom (S2) and the CH_2Cl_2 hydrogen atoms which were excluded due to the refinement problem. The final R1 = 0.0612 is based on 2631 "observed reflections" [$I > 2\sigma(I)$].

Results and Discussion

Alkoxide Precursors. We have demonstrated previously that alkyl nitrites (RON=O) add to (por)Ru(CO) complexes to generate the nitrosyl alkoxide (por)Ru(NO)(OR) trans addition products.[3,4,18−20] The $(por)Ru(NO)(O\text{-}i\text{-}C_5H_{11})$ complexes needed for this study were prepared similarly (Scheme 1) in 76% (por = TPP) and 62% (por = OEP) yields. The TTP analogue has been prepared previously.[3,4] The IR spectra of the alkoxide complexes as KBr pellets display bands at 1800 cm^{-1} (TPP) and 1788 cm^{-1} (OEP) attributed to ν_{NO}.

Monometallic Thiolate Complexes. The $(TPP)Ru(NO)(O\text{-}i\text{-}C_5H_{11})$ alkoxide complex reacts with excess ethane-1,2-dithiol in CH_2Cl_2 at room temperature to generate the monometallic thiolate−thiol derivative in 57% isolated yield as shown in Scheme 2. The previously reported $(TTP)Ru(NO)(O\text{-}i\text{-}C_5H_{11})$ alkoxide complex reacts similarly to produce its thiolate−thiol derivative in 61% isolated yield. The use of excess dithiol is necessary to minimize the formation of the bimetallic derivatives (see later).

The monometallic products of Scheme 2 are isolated as moderately air-stable green solids, showing no signs of decomposition in the solid state in air after a 1 week period. However,

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(18) Yi, G.-B.; Khan, M. A.; Powell, D. R.; Richter-Addo, G. B. *Inorg. Chem.* **1998**, *37*, 208−214.

(19) Richter-Addo, G. B. *Acc. Chem. Res.* **1999**, *32*, 529−536.

(20) Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1996**, *35*, 3453−3454.

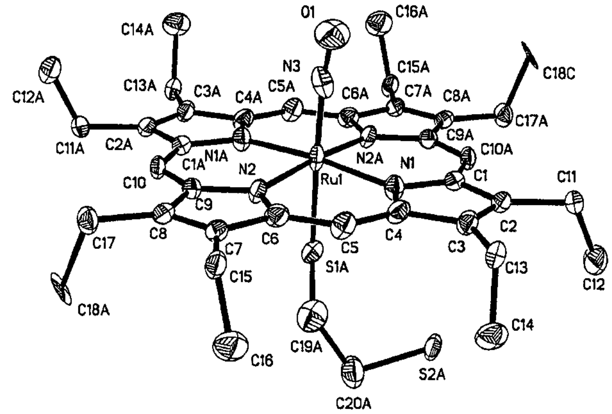
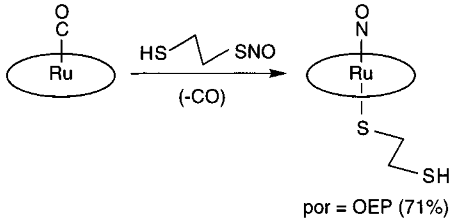


Figure 1. Molecular structure of (OEP)Ru(NO)(SCH$_2$CH$_2$SH). Only one of the disordered arrangement of the Ru and axial ligands is shown. Atoms are drawn with 50% thermal ellipsoids.

Scheme 3



their solutions are air-sensitive. These monometallic thiolate−thiol complexes are soluble in CH$_2$Cl$_2$ and benzene, but are insoluble in hexane. Their IR spectra (CH$_2$Cl$_2$) show bands at 1803 cm^{-1} (TPP) or 1793 cm^{-1} (TTP) due to ν_{NO}, and these are within the range observed for linear NO ligands in (por)-Ru(NO)-containing complexes. Their ^{1}H NMR spectra show, in addition to the signals for the porphyrin macrocycle, signals at ca. −2.3 ppm (t, SCH_2CH$_2$SH), −0.8 ppm (dt, SCH$_2$CH_2-SH), and −0.1 ppm (t, SCH$_2$CH$_2$SH) due to the coordinated thiolate−thiol ligands.

We were not successful in preparing (OEP)Ru(NO)(SCH$_2$-CH$_2$SH) by the alkoxide-thiolate exchange method described in Scheme 2. Hence, another preparative route was sought. The reaction of (OEP)Ru(CO) with the HSCH$_2$CH$_2$SNO reagent (generated in situ from the reaction of *t*-BuONO and ethane-1,2-dithiol) gives the desired product (Scheme 3) in 71% isolated yield via a formal trans addition of the RSNO across the metal center (cf. Scheme 1).

The ν_{NO} of 1793 cm^{-1} (CH$_2$Cl$_2$) of this purple product is identical to that of the TTP derivative, however, the peaks in the ^{1}H NMR spectrum due to the thiolate−thiol ligand in this OEP derivative are shifted slightly upfield by ca. 0.2−0.5 ppm from those of the tetraarylporphyrin analogues, with the greatest shift occurring for the RuSCH_2-hydrogens. Thus, the chemical shifts of the α-methylene protons of the thiolate−thiol groups (i.e., Ru-SCH_2CH$_2$SH) are similar in the TPP (−2.30 ppm) and TTP (−2.31 ppm) cases, but are upfield-shifted in the OEP case (−2.78 ppm).

To unambiguously confirm the identity of the thiolate−thiol derivatives, we undertook a single-crystal X-ray crystallographic study of a representative example, namely (OEP)Ru(NO)(SCH$_2$-CH$_2$SH), and the molecular structure is shown in Figure 1.

The axial NO and -SCH$_2$CH$_2$SH groups are completely disordered over both axial sites. The Ru atom is slightly (by 0.13 Å) vertically displaced from the 24-atom porphyrin plane toward the axial nitrosyl ligand, and this feature is not uncommon for nitrosyl porphyrins. Indeed, related axial displacements of the central metal in nitrosyl porphyrins toward the NO ligand have been observed for six-coordinate complexes such as (OEP)Os(NO)(O$_2$PF$_2$),[2] [(OEP)Os(NO)]$_2$(μ-O),[30] and (OEP)Ru(NO)(SCH$_2$CF$_3$).[21] The Ru−N(por) bond lengths in (OEP)Ru(NO)(SCH$_2$CH$_2$SH) are 2.047(4), 2.059(4), 2.061(4), and 2.090(4) Å. The Ru−N(O) and N−O bond lengths are 1.802(9) and 1.166(11) Å, respectively, and are within the ranges observed for other structurally characterized (por)Ru(NO)-containing complexes (see Table 8 in Supporting Information).[3,18,20−29] The Ru−N−O moiety is essentially linear, displaying an angle of 170.9(9)°. The axial Ru−S bond length is 2.316(4) Å, and the Ru−S−C bond angle is 111.0(4)°.

Table 1. Crystal Data and Structure Refinement

empirical formula	C$_{39}$H$_{51}$N$_5$OS$_2$Cl$_2$Ru
fw	841.94
diffractometer	Siemens P4
T, K	133(2)
crystal system	Monoclinic
space group	$P2_1/n$
unit cell dimensions	$a = 8.364(1)$ Å, $\alpha = 90°$ $b = 10.4150(11)$ Å, $\beta = 91.608(7)°$ $c = 22.570(2)$ Å, $\gamma = 90°$
V, *Z*	1965.3(4) Å^3, 2
D(calcd), g/cm^3	1.423
abs coeff, mm^{-1}	0.679
F(000)	876
crystal size	0.14 × 0.32 × 0.24 mm
θ range for data collection	1.81−25.00°
index ranges	$-9 \leq h \leq 0$, $-12 \leq k \leq 0$, $-26 \leq l \leq 26$
no. of reflctns collcd	3701
no. of indep reflcns	3444 [$R_{int} = 0.0324$]
max and min transmission	0.2620 and 0.2391
nos. of data/restraints/parameters	3435/25/286
goodness-of-fit on F^2	1.109
final *R* indices [$I > 2\sigma(I)$][a,b]	R1 = 0.0612, wR2 = 0.1426
R indices (all data)[a,b]	R1 = 0.0886, wR2 = 0.1697
largest diff. peak and hole	0.905 and −0.706 e Å^{-3}

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

The 3-carbon and 4-carbon thiolate complexes, namely (TTP)-Ru(NO)(SCH$_2$CH$_2$CH$_2$SH) (ν_{NO} 1779 cm^{-1}, KBr) and (TTP)-Ru(NO)(SCH$_2$CH$_2$CH$_2$CH$_2$SH) (ν_{NO} 1770 cm^{-1}, KBr), were prepared as green powders in 49% and 58% isolated yields, respectively, by the alkoxide-thiolate exchange method similar to that described in Scheme 2. The Ru−SCH_2− resonances for the three monometallic TTP complexes are slightly upfield shifted in the order edtH (−2.31) > pdtH (−2.55 ppm) > bdtH (−2.65 ppm).

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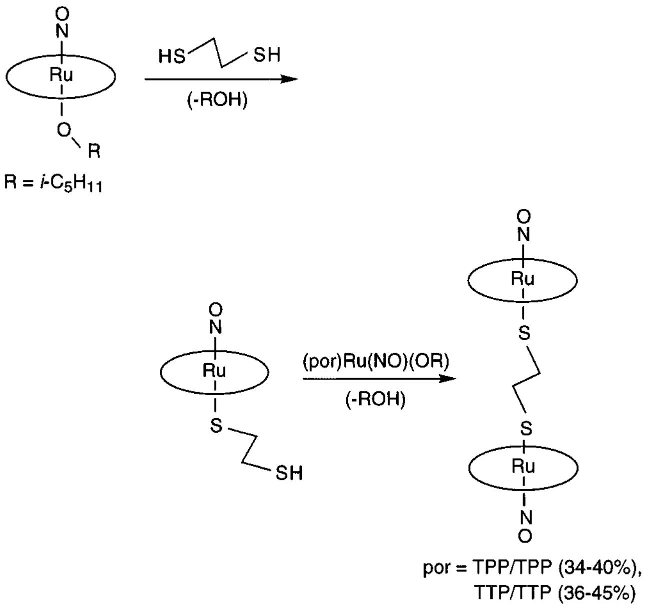
Scheme 4



Bimetallic μ-Dithiolate Complexes. Addition of a half equivalent of ethane-1,2-dithiol to the (por)Ru(NO)(O-*i*-C_5H_{11}) (por = TPP, TTP) precursors results in the generation of the symmetrical bimetallic μ-dithiolate derivatives. The reaction proceeds in two steps (as judged by ^{1}H NMR spectroscopy), with the first step producing the monometallic thiolate−thiol derivative (Scheme 4).

The final bimetallic products are isolated in low yields, partly due to the fact that the second step of the reaction is slow, and the bimetallic products are thermally sensitive and decompose in solution as the reaction progresses (the TPP/TPP complex is more prone to decomposition). Thus, we have found that a 4−6 h reaction period generally results in fair yields of the desired bimetallic products which are isolated as green solids after chromatography through silica gel (to separate them from their monometallic complexes). The bimetallic complexes are air-sensitive both in the solid state and in solution. They are soluble in CH_2Cl_2 and benzene, but are insoluble in hexane. The ν_{NO} values (CH_2Cl_2) are similar to those of their monometallic precursors. The most noticeable change between these bimetallic derivatives and their monometallic precursors lies in their ^{1}H NMR spectra. Importantly, the *single* peak for the μ-edt dithiolate ligands in both the symmetric TPP/TPP and TTP/TTP bimetallic derivatives lies at −5.73 ppm, which is shifted further upfield (by ~3.4 ppm) from the corresponding α-methylene signals in the monometallic precursors and reflects the contributions of the ring current effects from both porphyrins to the resonances of the bridging dithiolate protons.

We have also prepared the 3-carbon and 4-carbon bridged dithiolate derivatives of TTP. Interestingly, as the chain length of the bridging dithiolate ligand increases, the α-methylene proton ^{1}H NMR chemical shifts become similar to those of the monometallic complexes (i.e., less upfield shifted; Figure 2), indicative of the increased distance between these protons and the second (more distant) porphyrin. Furthermore, the signals for the central $-CH_2-$ protons are less upfield-shifted in the order μ-edt (−5.73 ppm) < μ-pdt (−4.64 ppm) < μ-bdt (−3.11 ppm) as seen in Figure 2, indicating that they are less influenced by the ring currents of the two porphyrin units due to increased distances between these protons and the porphyrin rings.

As was the case with the monometallic OEP thiolate−thiol complex, we were not able to prepare the OEP/OEP bimetallic derivative by the alkoxide-thiolate exchange reaction of Scheme 4. Rather, we employed a variation of the formal trans addition reaction of RSNO to (OEP)Ru(CO) to attain this synthetic objective. Thus, reaction of (OEP)Ru(NO)(SCH_2CH_2SH) with *tert*-butyl nitrite followed by addition of (OEP)Ru(CO) to the reaction solution generates the OEP/OEP bimetallic μ-dithiolate complex in 36% isolated yield (Scheme 5). We have not been able to isolate the putative (OEP)Ru(NO)(SCH_2CH_2SNO) complex: it is very air-sensitive and thermally unstable. However, its formation was inferred from its subsequent reaction with (OEP)Ru(CO) to give the desired bimetallic OEP/OEP product of Scheme 5, namely [(OEP)Ru(NO)]$_2$(μ-edt-*S*,*S*′).

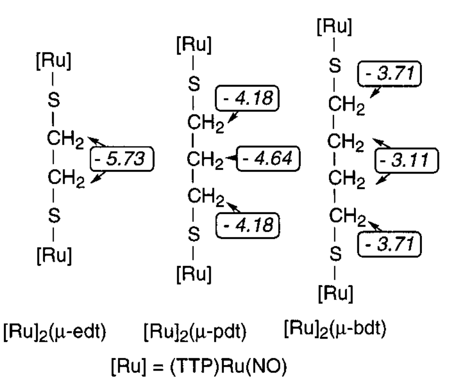
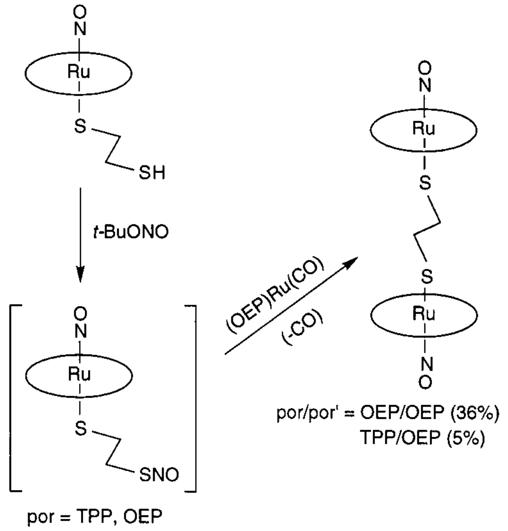


Figure 2. Proton chemical shifts of [(TTP)Ru(NO)]$_2$(μ-dithiolate) complexes (in $CDCl_3$).

Scheme 5



The ^{1}H NMR spectrum of the OEP/OEP derivative reveals a resonance at −6.20 ppm attributed to the dithiolate methylene protons. This represents an upfield shift of 0.47 ppm from the analogous TPP/TPP derivative and is almost identical to the 0.48 ppm upfield shift observed for the methylene protons in the monometallic (por)Ru(NO)(SCH_2CH_2SH) complexes when the OEP derivative (δ −2.78 ppm) is compared with the TPP (δ −2.30 ppm) analogue.

We successfully extended this methodology (Scheme 5) to the synthesis of the unsymmetrical mixed TPP/OEP bimetallic complex. Thus, reaction of (TPP)Ru(NO)(SCH_2CH_2SH) with *tert*-butyl nitrite followed by reaction with (OEP)Ru(CO) results in the formation of [(TPP)Ru(NO)](μ-edt-*S*,*S*′)[Ru(NO)(OEP)] in very low isolated yields (ca. 5%). The symmetrical bimetallic complexes, namely [(OEP)Ru(NO)]$_2$(μ-edt-*S*,*S*′) and [(TPP)Ru(NO)]$_2$(μ-edt-*S*,*S*′) were also formed as byproducts, and their similar solubilities to that of the desired mixed bimetallic posed

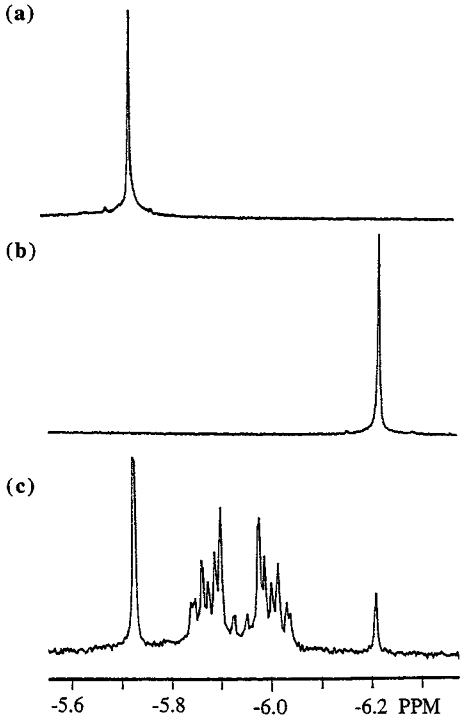


Figure 3. Upfield region of the 300 MHz ^{1}H NMR spectra of (a) $[(TPP)Ru(NO)]_2$(*μ*-edt-*S,S′*), (b) $[(OEP)Ru(NO)]_2$(*μ*-edt-*S,S′*), and (c) the product mixture obtained during the preparation of [(TPP)Ru(NO)]-(*μ*-edt-*S,S′*)[Ru(NO)(OEP)].

an impediment to obtaining sizable quantities of elementally pure [(TPP)Ru(NO)](*μ*-edt-*S,S′*)[Ru(NO)(OEP)]. We have also found that we got better yields (although still low) of the TPP/OEP bimetallic product if we started the sequential reaction shown in Scheme 5 using (TPP)Ru(NO)(SCH_2CH_2SH): i.e., addition of *tert*-butyl nitrite to (TPP)Ru(NO)(SCH_2CH_2SH) followed by addition of (OEP)Ru(CO), rather than addition of *tert*-butyl nitrite to (OEP)Ru(NO)(SCH_2CH_2SH) followed by addition of (TPP)Ru(CO). This is consistent with our earlier observations that RSNO additions to (OEP)Ru(CO) were cleaner than the analogous additions to (TPP)Ru(CO).[3,4,19]

A representative 300 MHz ^{1}H NMR spectrum of the crude product mixture of the TPP/OEP mixed bimetallic preparation, showing only the region containing the resonances of the bridging thiolate protons, is shown in Figure 3c. The single peak at −5.73 ppm is due to $[(TPP)Ru(NO)]_2$(*μ*-edt-*S,S′*) (Figure 3a), whereas the single peak at −6.20 ppm is due to $[(OEP)Ru(NO)]_2$(*μ*-edt-*S,S′*) (Figure 3b). The plethora of peaks in the center region is assigned to the bridging methylene protons of the unsymmetrical [(TPP)Ru(NO)](*μ*-edt-*S,S′*)[Ru(NO)(OEP)] complex, and these protons display an AA′BB′ coupling pattern.[31] The 400 MHz ^{1}H NMR spectrum for these methylene protons is shown in Figure 4a. The computer simulation of this pattern is shown in Figure 4b and gives $J_{AB'} = J_{A'B} = 11.2$ Hz, $J_{AA'} = J_{BB'} = -12.2$ Hz, $J_{AB} = 5$ Hz, $J_{A'B'} = 3.7$ Hz, and $\Delta\upsilon_{AB} = 51$ Hz. Needless to say, we believe that it is the presence of two distinctly different porphyrins in this novel TPP/OEP derivative that causes the inequivalence of the *μ*-edt protons.

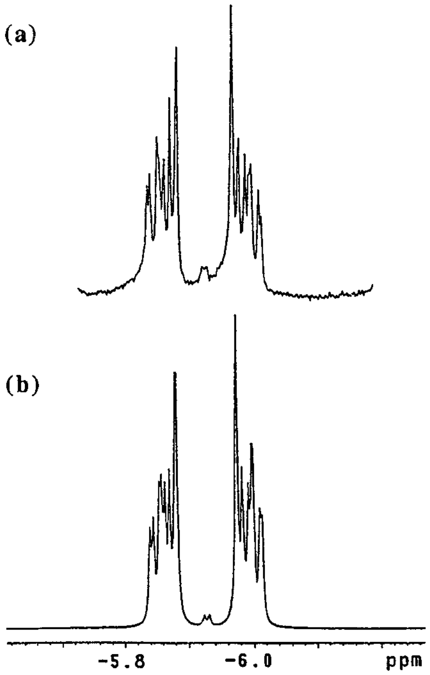


Figure 4. Upfield region of the 400 MHz ^{1}H NMR spectrum of [(TPP)-Ru(NO)](*μ*-edt-*S,S′*)[Ru(NO)(OEP)]: (a) experimental spectrum (sample in $CDCl_3$); (b) computer simulation.

In summary, we have prepared monometallic thiolate−thiol complexes of ruthenium nitrosyl porphyrins, and have also prepared their novel bimetallic *μ*-dithiolate derivatives. To the best of our knowledge, these are the first examples of *μ*-dithiolate complexes reported for any metalloporphyrin. These symmetrical and unsymmetrical bimetallic complexes represent an interesting new class of compounds for further study in which electron-donating and -withdrawing effects of the (por)Ru units (coupled with the varied dithiolate chain length) can be fine-tuned to alter the oxidation chemistry and electrophilic addition reactions of the *μ*-dithiolate ligands. Efforts are currently underway to explore such reactivity.

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Supporting Information Available: Drawings for (OEP)Ru(NO)-(SCH_2CH_2SH) and listings of crystal data, atomic coordinates, anisotropic displacement parameters, bond lengths and angles, hydrogen coordinates and isotropic displacement parameters, torsion angles, least squares planes, and a table of structurally characterized ruthenium nitrosyl porphyrins. This material is available free of charge via the Internet at http://pubs.acs.org.

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