that make up complex **3** is a scalene triangle and spin frustration results.

It should be possible to prepare additional polynuclear iron and manganese complexes that have ground states with large numbers of unpaired electrons. This can be done by designing the polynuclear complex so that it exhibits spin frustration. The complex $[Mn^{IV}_4Mn^{III}_8O_{12}(O_2CPh)_6(H_2O)_4]$ probably also has a $S = 14$ ground state due to spin frustration.[8f,22,36]

**Note Added in Proof.** For a recent report of the preparation of diimidazole **1**, see: Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210.

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**Supplementary Material Available:** Tables of complete bond lengths and bond angles, anisotropic thermal parameters, calculated hydrogen atom positions, and magnetic susceptibility data and a stereoview of complex **3**·$8CH_2Cl_2$ (10 pages); a listing of observed and calculated structure factors for complex **3**·$8CH_2Cl_2$ (20 pages). Ordering information is given on any current masthead page.

# Nitridoosmium(VI) and Nitridoruthenium(VI) Complexes of Cysteine(2-) and Related Ligands

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**Abstract:** Anionic complexes of nitridoruthenium(VI) and nitridoosmium(VI) containing covalently bound *N*-acetyl-L-cysteinato, 3-sulfidopropionato, and 3-sulfidopropionamidato ligands have been synthesized to model the binding of δ-(L-α-aminoadipyl)-L-cysteinyl-D-valine to the iron center in the metalloenzyme isopenicillin N synthetase. The complexes are prepared by the reaction of *N*-acetyl-L-cysteine, 3-mercaptopropionic acid, and 3-mercaptopropionamide with $[NBu^n_4][Os(N)(OSiMe_3)_4]$, $[NBu^n_4][Os(N)Cl_4]$, $[NBu^n_4][Ru(N)(CH_2SiMe_3)_4]$, or $[NBu^n_4][Ru(N)(OSiMe_3)_4]$. They have been characterized by elemental analysis and IR and NMR spectroscopy. Spectroscopic data show that the *N*-acetyl-L-cysteinato and 3-sulfidopropionato ligands are bound to the metal center through sulfur and oxygen, while the 3-sulfidopropionamidato ligands are bound through sulfur and nitrogen. The molecular structures of *cis*-$[NBu^n_4][Os(N)(O_2CCH_2CH_2S)_2]$, $[NBu^n_4][Os(N)\{O_2CCH(NHCOCH_3)CH_2S\}_2]$, and $[PPh_4][Ru(N)(NHCOCH_2CH_2S)_2)]$ were determined by single-crystal X-ray diffraction. These complexes were found to have distorted square-pyramidal geometry around the metal center. *cis*-$[NBu^n_4][Os(N)(O_2CCH_2CH_2S)_2]$ crystallizes in monoclinic space group $P2_1/c$ with $a = 13.718$ (6) Å, $b = 10.080$ (3) Å, $c = 19.890$ (5) Å, $\beta = 92.16$ (3) Å, and $Z = 4$. $[NBu^n_4][Os(N)\{L\text{-}O_2CCH(NHCOCH_3)CH_2S\}_2]$ crystallizes in monoclinic space group $C2$ with $a = 18.371$ (6) Å, $b = 9.261$ (1) Å, $c = 21.125$ (7) Å, $\beta = 102.92$ (3) Å, and $Z = 4$. $[PPh_4][Ru(N)(NHCOCH_2CH_2S)_2)]$ crystallizes in orthorhombic space group *Pbca* with $a = 23.022$ (1) Å, $b = 16.120$ (1) Å, $c = 15.728$ (1) Å, and $Z = 8$.

## Introduction

The biological importance of metal-cysteine interactions has led to a great deal of activity in the study of the coordination chemistry of cysteine and related molecules. Coordination of cysteine to a metal center has been shown to occur in a number of metalloenzymes. These include enzymes involved in the synthesis of β-lactam antibiotics, such as isopenicillin N synthetase,[1] and those causing the decomposition of these antibiotics, such as β-lactamase II.[2] Present evidence suggests that the first step in the oxidative cyclization of δ-(L-α-aminoadipoyl)-L-cysteinyl-D-valine to isopenicillin N is the coordination of the substrate to the iron atom, through the cysteinyl sulfur and the valinyl amide nitrogen. Coordination of the cysteine thiolate to an iron center is known to occur in cytochrome P-450,[3] ω-hydroxyase,[4] chloroperoxidase,[5] subunit II of bovine cytochrome *c* oxidase,[6] and iron-sulfur electron transport proteins.[7]

Main group metal and transition metal complexes of cysteine and cysteine derivatives have been prepared and isolated.[8] In general, these are insoluble or sparingly soluble materials and have been characterized mainly by elemental analysis and IR spectroscopy. On the basis of their infrared spectra, these complexes were proposed to have monodentate (S), bidentate (N,S), bidentate (O,S), tridentate (O,N,S), or bridging bonding modes.[9] The

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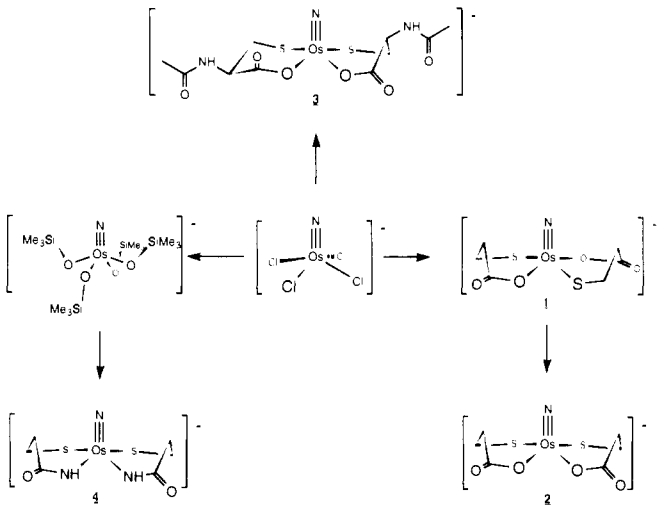
structures of cysteine complexes of Co(III), Pd(II), Mo(IV), Mo(V), and W(V) were shown to have bidentate (N,S) or tridentate (O,S,N) coordination by X-ray diffraction.[10]

The importance of cysteine in biological systems can probably be ascribed to the chemical reactivity of the thiol group, which is capable of both acid/base and oxidation/reduction chemistry. Extensive studies into the redox behavior of the SH group exist in the literature, particularly its oxidation by metal ions.[11] Much of the data collected on the mechanism of this oxidation involves the use of Fe(III) and Cu(II) and points to the formation of transient metal–cysteine complexes, followed by the oxidation of the sulfur.[12,13] High oxidation state metal complexes of cysteine are usually difficult to prepare because of this facile oxidation of cysteine by oxidized metal ions.

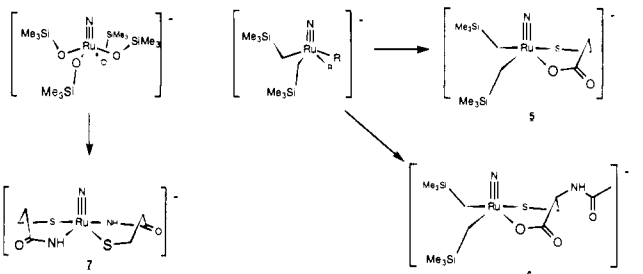
Despite the extensive studies on metal ion complexes of cysteine and its related derivatives, there is no conclusive evidence for the formation of S,O chelates of cysteine with transition metals. The existence of thermally unstable, monomeric S,O cysteine chelates of Fe(III) was proposed on the basis of studies in frozen solutions.[14] However, other workers have suggested that the solution species are actually polymers with tridentate (N,O,S) coordination of cysteine.[15] Coordination of the cysteine to the metal through sulfur and oxygen probably occurs in aqueous solutions of In(III)[16] and Zn(II)[17] at low pH when the amino group is protonated.

We have shown, in previous work, that it is possible to prepare stable thiolate complexes of high oxidation state osmium and ruthenium. The osmium(VI) and ruthenium(VI) complexes *cis*-$[NBu^n_4][Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]$, *cis*-$[Os(N)(CH_2SiMe_3)_2(2\text{-}S\text{-}NC_5H_4)]_2$,[18] $[NBu^n_4][Os(N)(SCH_2CH_3)_4]$, and $[NBu^n_4][Ru(N)(SCH_2CH_3)_4]$[19] are prepared without oxidation of the thiolate. Tetrathiolato complexes $Ru(SC_{10}H_{13})_4(CH_3CN)$, $Os(SC_{10}H_{13})_4(CH_3CN)$, $Os(SC_{15}H_{23})_4(CH_3CN)$, and $Ru(SC_{15}H_{23})_4(CH_3CN)$ of ruthenium and osmium(IV) have also been prepared.[20]

**Scheme I.** Synthesis of Osmium Complexes **1–4**



**Scheme II.** Synthesis of Ruthenium Complexes **5–7**



In this paper we report the synthesis and characterization of stable, high oxidation state complexes of osmium and ruthenium with covalently bound 3-sulfidopropionato, *N*-acetyl-L-cysteinato, and 3-sulfidopropionamidato ligands. The molecular structures of three of these complexes are also reported. These are the first cysteine complexes of ruthenium and osmium. The coordination modes of these ligands to the oxidized metal centers may be similar to that in the active sites of certain non-heme, iron enzymes, such as isopenicillin N synthase.

## Results and Discussion

**Synthesis of Osmium(VI) and Ruthenium(VI) Complexes.** We have been able to prepare osmium and ruthenium complexes containing the dianions of *N*-acetyl-L-cysteine, 3-mercaptopropionic acid, and 3-mercaptopropionamide. All of these complexes have been isolated and characterized by elemental analysis and IR, $^1H$ NMR, and $^{13}C$ NMR spectroscopy. They are thermally stable and are stable to air. The sulfur-containing ligands are not oxidized by the high oxidation state metal centers.

The osmium complexes *trans*-$[NBu^n_4][Os(N)\{SCH_2CH_2C(O)O\}_2]$ (**1**), *cis*-$[NBu^n_4][Os(N)\{SCH_2CH_2C(O)O\}_2]$ (**2**), and $[NBu^n_4][Os(N)\{SCH_2CH(NHCOCH_3)C(O)O\}_2]$ (**3**) are prepared by the reaction between $[NBu^n_4][Os(N)Cl_4]$ and 3-mercaptopropionic acid or *N*-acetyl-L-cysteine in the presence of triethylamine. In a typical preparation, a dichloromethane solution containing 2 equiv of *N*-acetyl-L-cysteine or 3-mercaptopropionic acid and 4 equiv of triethylamine is added dropwise to a cold solution of $[NBu^n_4][Os(N)Cl_4]$. Small crystals of analytically

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Table I: Selected Bond Distances (Å) for 2, 3, and 7b

| 2 | | 3 | | 7b | |
|---|---|---|---|---|---|
| Os-N1 | 1.608 (7) | Os-N | 1.63 (1) | Ru-N3 | 1.595 (8) |
| Os-S1 | 2.289 (2) | Os-S1 | 2.299 (4) | Ru-S1 | 2.324 (3) |
| Os-S2 | 2.285 (2) | Os-S2 | 2.304 (5) | Ru-S2 | 2.306 (3) |
| Os-O1 | 2.045 (5) | Os-O1 | 2.002 (8) | Ru-N1 | 2.021 (8) |
| Os-O2 | 2.020 (5) | Os-O4 | 2.00 (1) | Ru-N2 | 2.02 (1) |
| C3-O1 | 1.304 (9) | C3-O1 | 1.32 (2) | C1-N1 | 1.35 (1) |
| C3-O3 | 1.203 (9) | C3-O2 | 1.20 (2) | C1-O1 | 1.24 (1) |
| C6-O2 | 1.322 (9) | C8-O4 | 1.34 (2) | C4-N2 | 1.31 (1) |
| C6-O4 | 1.179 (10) | C8-O5 | 1.21 (3) | C4-O4 | 1.22 (1) |

Table II: Selected Bond Angles (deg) for 2, 3, and 7b

| 2 | | 3 | | 7b | |
|---|---|---|---|---|---|
| S1-Os-S2 | 81.76 (7) | S1-Os-O1 | 92.2 (3) | S1-Ru-N1 | 91.0 (3) |
| O1-Os-O2 | 76.9 (2) | S2-Os-O1 | 78.7 (4) | S2-Ru-N1 | 81.2 (2) |
| S1-Os-O1 | 90.9 (1) | S1-Os-O4 | 78.9 (3) | S1-Ru-N2 | 79.5 (3) |
| S2-Os-O2 | 91.1 (2) | S2-Os-O4 | 91.1 (3) | S2-Ru-N2 | 90.2 (3) |
| S1-Os-N1 | 105.1 (3) | S1-Os-N | 110.4 (6) | S1-Ru-N3 | 109.7 (3) |
| S2-Os-N1 | 106.2 (3) | S2-Os-N | 111.9 (6) | S2-Ru-N3 | 107.1 (3) |
| O1-Os-N1 | 107.8 (3) | O1-Os-N | 100.6 (8) | N1-Ru-N3 | 104.2 (4) |
| O2-Os-N1 | 108.2 (3) | O4-Os-N | 105.9 (6) | N2-Ru-N3 | 104.6 (4) |
| O1-C3-O3 | 121.2 (7) | O1-C3-O2 | 120 (1) | O1-C1-N1 | 122.9 (9) |
| O2-C6-O4 | 122.2 (7) | O4-C8-O5 | 121 (2) | O4-C4-N2 | 125 (1) |

pure **1**, **2**, or **3** are obtained by vapor diffusion of diethyl ether into a concentrated dichloromethane solution at −30 °C. The orange trans isomer and the yellow cis isomer of $[NBu^n_4][Os(N)\{SCH_2CH_2C(O)O\}_2]$ are obtained in 62% and 13% yield, respectively, as crystalline complexes. The trans isomer is the kinetic product and can be converted thermally to the cis isomer.

The ruthenium complexes $[NBu^n_4][Ru(N)(CH_2SiMe_3)_2\{SCH_2CH_2C(O)O\}]$ (**5**) and $[NBu^n_4][Ru(N)(CH_2SiMe_3)_2\{SCH_2CH(NHCOCH_3)C(O)O\}]$ (**6**) are prepared by protonolysis of two of the alkyl ligands in $[NBu^n_4][Ru(N)(CH_2SiMe_3)_4]$ with 3-mercaptopropionic acid and *N*-acetyl-L-cysteine, respectively. We have previously shown that the anionic alkyl complexes $[Os(N)R_4]^-$ and $[Ru(N)R_4]^-$ react with HCl to give *cis*-$[M(N)R_2Cl_2]^-$.[21] Presumably, the carboxylic acid and sulfhydryl protons cleave the alkyl ligands with resultant coordination of the sulfur and oxygen to give the observed products and tetramethylsilane. Both **5** and **6** are stable to water and can be purified on silica gel. The tetraphenylphosphonium salts of these complexes are prepared in a similar manner from $[PPh_4][Ru(N)(CH_2SiMe_3)_4]$.

Coordination of the tripeptide δ-(L-α-aminoadipyl)-L-cysteinyl-D-valine to the iron center in isopenicillin N synthetase is proposed to occur both through the cysteine sulfur atom and the valine amide nitrogen.[22] Metal complexes containing amides coordinated through the amide nitrogen are known. Most of these involve the coordination of dipeptides, tripeptides, and small oligopeptides to divalent copper, nickel, and palladium.[23] 3-Sulfidopropionamidato complexes of osmium(VI) and ruthenium(VI) were synthesized to show that bonding through an amide nitrogen is possible in high-valent complexes of the iron triad metals. The trimethylsiloxide complexes $[NBu^n_4][M(N)(OSiMe_3)_4]$ (M = Os, Ru) react with 3-mercaptopropionamide to give $[NBu^n_4][Os(N)\{SCH_2CH_2C(O)NH\}_2]$ (**4**) and $[NBu^n_4][Ru(N)\{SCH_2CH_2C(O)NH\}_2]$ (**7**) in yields of approximately 40% after column chromatography and recrystallization. The tetraphenylphosphonium salt of **7** is prepared in a similar way.

**Molecular Structure Determination of Complexes 2, 3, and 7b.** The structures of *cis*-$[NBu^n_4][Os(N)(O_2CCH_2CH_2S)_2]$ (**2**) $[NBu^n_4][Os(N)(\{O_2CCH(NHCOCH_3)CH_2S\}_2]$ (**3**), and $[PPh_4][Ru(N)(NHCOCH_2CH_2S)_2]$ (**7b**) were determined by single-crystal X-ray diffraction analysis (Figures 1–3). These complexes are yellow, crystalline materials. The ligands in all three complexes are coordinated to the metal in a bidentate fashion. The 3-sulfidopropionato and *N*-acetyl-L-cysteinato ligands in **2** and **3** are coordinated to the osmium through sulfur and oxygen, while the 3-sulfidopropionamidato ligands in **7b** are coordinated to the ruthenium through sulfur and the amide nitrogen. The ligands in **2** and **3** are bound in a σ fashion through only one of the carboxyl oxygens. This is clearly shown by the O–C bond distances summarized in Table I. In **2**, the two chelating ligands are in a cis configuration, so that each sulfur is trans to an oxygen,

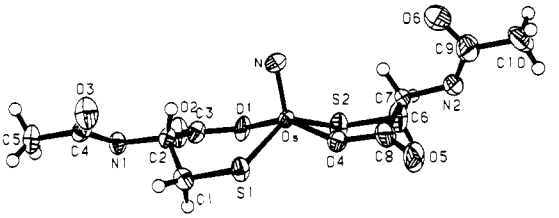


Figure 1. ORTEP diagram of $[Os(N)\{O_2CCH(NHCOCH_3)CH_2S\}_2]^-$.

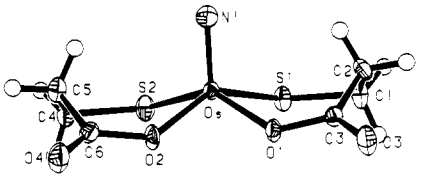


Figure 2. ORTEP diagram of $[Os(N)(O_2CCH_2CH_2S)_2]^-$.

whereas the ligands in **3** and **7b** are in a trans configuration. The geometry around the metal is distorted square-pyramidal in all cases, with the metal slightly above the plane of the four basal ligands. Distortions of this type have been found in other nitridoruthenium(VI) and nitridoosmium(VI) complexes and are ascribed to the repulsion between metal–nitrogen π-bonding electrons, localized on the metal, and σ-bonding electrons to the ligands.[24] The ligand–metal–ligand angles are summarized in Table II.

Each chelating ligand forms a six-membered metallocycle with the metal. These metallocycles are in a boat conformation in all three complexes. The boat form may be favored because the sulfur and osmium atoms in the ring expand its size, reducing the trans-annular strain, and because there are no eclipsing interactions. Certain six-membered heterocycles adopt a boat or twist-boat conformation.[25]

The *N*-acetyl-L-cysteine complex **3** crystallizes in the *C*2 space group. Two molecules of dichloromethane were found per unit cell. As stated above, the *N*-acetyl-L-cysteine ligands coordinate in a bidentate fashion, and the oxygen and sulfur atoms are trans to one another. The six-membered metallocycles are in a boat conformation, and the anion as a whole has no symmetry elements other than a $C_1$ axis. As a consequence of this geometry, the metal center is chiral. Since there is an asymmetric center on each of the *N*-acetyl-L-cysteinato ligands, two diastereomers are possible with a trans configuration at the metal center. The data crystal contained one diastereomer exclusively. Examination of the $^1H$ NMR spectrum of the crude reaction mixture shows that only trace quantities of the other diastereomer are produced. Intermolecular O–N distances of 3.01 (2) and 2.79 (3) Å suggest possible hydrogen bonding between the amide proton in the acetyl group of one anion and the carbonyl oxygen in the acetyl group of an adjacent anion.

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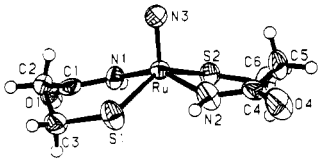


**Figure 3.** ORTEP diagram of $[Ru(N)(NHCOCH_2CH_2S)_2]^-$.

The 3-sulfidopropionato complex **2** crystallizes in the $P2_1/c$ space group. The oxygen and sulfur atoms are cis to one another. The complex has one $\sigma_v$ containing the Os–N bond and bisecting the S–Os–O angles, and thus it has approximate $C_s$ symmetry. The average N–Os–L angle of 107° compares with the angle of 103° in $[Os(N)Cl_4]^-$ and 107° in $[Os(N)R_4]^-$.[23,26] The Os and N1 atoms were disordered in two positions with a major site occupancy 0.922 (2). In the site of greatest occupancy, the metallocycle formed by each ligand is in a boat conformation. In the other site, the ligands are in the same position, but the Os–N bond is inverted, putting the metallocycle in a chair conformation. The Os–N distance of 1.608 (7) Å is slightly shorter than the Os–N distances of 1.63 (1) Å in **3**, 1.62 (1) Å in $[NBu^n_4][Os(N)(CH_2Si(CH_3)_3)_2(WS_4)]$,[27] 1.64 (1) and 1.62 (1) Å in $[Os(N)(CH_2Si(CH_3)_3)_2(S\text{-}C_5H_4N)]_2$,[28] and 1.614 Å in $[NBu^n_4][Os(N)Cl_4]$.[23]

The 3-sulfidopropionamidato complex **7b** crystallizes in the space group *Pbca*. The sulfur and nitrogen atoms occupy trans positions with N–Ru–S angles of 90.6°. Each amide group is clearly bound $\eta^1$ through the nitrogen atom. The amide protons were located and refined in the final structure. There is no distortion of the amide group; no lengthening or shortening of the C–N or C–O bonds is observed; the torsion angles for the H–N–C–O group show that the amide functionality remains essentially planar.

The other high oxidation state metal complexes of cysteine derivatives were prepared from aqueous sodium molybdate and tungstate solutions.[29] X-ray crystal structures of both [(cysteine methyl ester)$Mo(O)]_2$-$\mu$-$(O)_2$[30] and [(cysteine methyl ester)-$Mo(O)]_2$-$\mu$-$(S)_2$[31] show the cysteine esters to be coordinated to the molybdenum through the amino nitrogen and the thiolato sulfur, while the molecular structure of $Na_2Mo_2O_4(cysteine)_2 \cdot 5H_2O$ shows N,S,O coordination of the cysteine to each molybdenum center.[32] The Mo–S distances in [(cysteine ethyl ester)$Mo(O)]_2$-$\mu$-$(O)_2$ are 2.393 (8) and 2.378 (7) Å, and the Mo–S distance in $Na_2Mo_2O_4(cysteine)_2 \cdot 5H_2O$ is 2.49 Å. The W–S distances in $[W_2O_2S_2(cysteine)_2]^{2-}$ are 2.477 (5) and 2.549 (5) Å. The cysteinyl oxygen–metal distances vary from 2.22 (2) to 2.29 (2) Å in $[Mo_2O_4(cysteinyl)_2]^{2-}$ and $[W_2O_2S_2(cysteinyl)_2]^{2-}$.

**Spectroscopic Studies.** All of the complexes reported here been characterized by $^1H$ NMR, $^{13}C$ NMR, and IR spectroscopy. The $^1H$ NMR spectra are consistent with bidentate coordination of the *N*-acetyl-L-cysteinato, 3-sulfidopropionato, or 3-sulfidopropionamidato ligand. The spectra of **2**, **3**, **4**, and **7** show a second-order splitting pattern of the methylene protons consistent with an ABCD spin system, resulting from the asymmetry imposed by the apical nitride and bidentate coordination of these ligands. In the complexes containing (trimethylsilyl)methyl ligands, all of the methylene protons on the (trimethylsilyl)methyl group are inequivalent giving rise to a set of four doublets, while the trimethylsilyl groups are split into two singlets which is, again, consistent with the bidentate coordination of the cysteinato or 3-sulfidopropionato ligand. The amide proton in **4** and **7** appears as a broadened singlet in the $^1H$ NMR near 6 ppm. In the $^{13}C$ NMR the carbonyl carbons in all the complexes resonate near 180 ppm. The C2 and C3 carbon of the coordinated 3-sulfidopropionato and 3-sulfidopropionamidato ligand are approximately 40 and 26 ppm, respectively, and approximately 55 and 30 ppm in the coordinated *N*-acetyl-L-cysteinato ligand.

The infrared spectra show a single, strong absorption for the carbonyl group near 1660 $cm^{-1}$ for complexes **1**, **2**, and **6**. The lack of strong symmetric and asymmetric C–O stretching bands, characteristic of $\eta^3$-carboxylate coordination, is evidence for $\eta^1$-carboxylate coordination. Both **5** and **7** have a strong, single carbonyl absorption at 1603 $cm^{-1}$. The nitrido–metal stretching vibration in nitridoosmium(VI) and nitridorutehnium(VI) is sensitive to the donor ability of the ancillary ligands. In complexes **1–7**, this band is found between 1078 and 1095 $cm^{-1}$, indicating that the ligands are good donors to the metal.

## Conclusion

High oxidation state complexes of cysteine and related ligands have been synthesized and completely characterized by a variety of spectroscopic techniques and elemental analysis. The complexes of *N*-acetyl-L-cysteine and 3-sulfidopropionate are discrete monomers with bidentate coordination of the ligands through sulfur and oxygen. 3-Sulfidopropionamidato ligands bond through the sulfur and amide nitrogen atoms. Both the structural and spectroscopic studies show that the ligands chelate to the metals and six-membered rings are formed. The syntheses proceed without oxidation of the thiolate sulfur. Furthermore, the ability of an amide nitrogen to bind to a high oxidation state metal center has been demonstrated. The coordination of 3-sulfidopropionamidato to these oxidized iron triad metals may be similar to the coordination of δ-(L-α-aminoadipoyl)-L-cysteinyl-D-valine to iron in the metalloenzyme isopenicillin N synthetase. We are presently investigating the reaction chemistry of these new complexes with two-electron donors, electrophiles, and strong bases.

## Experimental Section

**Materials and Methods.** Proton NMR spectra were recorded on a General Electric QE-300 NMR spectrometer operating at 300 MHz or a Varian XL-200 NMR spectrometer operating at 200 MHz. $^{13}C$ NMR spectra were recorded on a General Electric QE-300 NMR spectrometer operating at 75.45 MHz or a General Electric GN500 NMR spectrometer operating at 125.76 MHz. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer. Microanalyses were performed by the School of Chemical Sciences Microanalytical Laboratory. Melting point determinations were performed on a Mel-Temp II capillary melting point apparatus.

***trans*-$[NBu^n_4][Os(N)(CO_2CH_2CH_2S)_2]$ (1).** A solution of 0.42 μL (0.48 mmol) of mercaptopropionic acid and 133 μL (0.96 mmol) of $Et_3N$ in 10 mL of $CH_2Cl_2$ were added dropwise with magnetic stirring to a cold (−30 °C) solution of 0.140 g (0.24 mmol) of $[NBu^n_4][Os(N)Cl_4]$ in 30 mL of $CH_2Cl_2$. The solution turned from pink to bright yellow instantly. The volume was reduced to 5 mL in vacuo, and the solution was placed in the freezer. Diethyl ether was added, and the resulting $Et_3NHCl$ was removed by filtration. Light orange crystals formed which were dried in vacuo to yield 0.097 g (62%): mp 118–118.5 °C; $^1H$ NMR (300 MHz, $CD_3CN$, 18 °C) δ 3.4 (m, 2 H, $CO_2CH_2CH_2S$), 3.07 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 2.95 (m, 4 H, $CO_2CH_2CH_2S$), 2.7 (m, 2 H, $CO_2CH_2CH_2S$), 1.58 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 1.33 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 0.95 (t, 12 H, $NCH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CD_3CN$, 18 °C) δ 13.77 ($NCH_2CH_2CH_2CH_3$), 20.30 ($NCH_2CH_2CH_2CH_3$), 24.29 ($NCH_2CH_2CH_2CH_3$), 27.24 ($CO_2CH_2CH_2S$), 40.86 ($CO_2CH_2CH_2S$), 59.30 ($NCH_2CH_2CH_2CH_3$), 179.34 ($CO_2CH_2CH_2S$); IR (KBr, $cm^{-1}$) 2959, 2870, 1659 ($\nu_{C-O}$), 1485, 1327, 1263, 1161, 1130, 1082 ($\nu_{NOs}$), 1020. Anal. Calcd for $OsC_{22}H_{44}O_4N_2S_2$: C, 40.35; H, 6.77; N, 4.28. Found: C, 40.36; H, 6.80; N, 4.19.

***cis*-$[NBu^n_4][Os(N)(CO_2CH_2CH_2S)_2]$ (2).** Yellow crystals of **2** were produced (0.020 g, 13%) by vapor diffusion of diethyl ether into the solution above, over a period of several weeks: mp 128–128.5 °C; $^1H$ NMR (300 MHz, $CD_3CN$, 18 °C) δ 3.2 (m, 2 H, $CO_2CH_2CH_2S$), 3.07 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 2.95, (m, 4 H, $CO_2CH_2CH_2S$), 2.76 (m, 2 H, $CO_2CH_2CH_2S$), 1.58 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 1.33 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 0.95 (t, 12 H, $NCH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (75.48 MHz, $CD_3CN$, 18 °C) δ 13.68 ($NCH_2CH_2CH_2CH_3$), 20.23 ($NCH_2CH_2CH_2CH_3$), 24.18 ($NCH_2CH_2CH_2CH_3$), 28.92 ($CO_2CH_2CH_2S$), 41.27 ($CO_2CH_2CH_2S$), 59.22 ($NCH_2CH_2CH_2CH_3$), 177.57 ($CO_2CH_2CH_2S$); IR (KBr, $cm^{-1}$) 2961, 2684, 1670 ($\nu_{C-O}$), 1471, 1331, 1262, 1164, 1100, 1092 ($\nu_{NOs}$), 916. Anal. Calcd for $OsC_{22}H_{44}O_4N_2S_2$:

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C, 40.35; H, 6.77; N, 4.28. Found: C, 40.59; H, 6.85; N, 4.16.

**Isomerization of *trans*- to *cis*-[$NBu^n_4$][Os(N)($CO_2CH_2CH_2S$)$_2$].** A solution of 0.004 g of [$NBu^n_4$][Os(N)($C_3H_4O_2S$)$_2$] in 0.6 mL of $CD_3CN$ was added to a 5-mm NMR tube and the tube was flame sealed under vacuum. An initial NMR spectrum showed only **1**. The sample was placed in a glass sleeve and heated in an oil bath at 80 °C for 1.75 h. A second $^1H$ NMR spectrum showed that the sample consisted of a mixture of **1** and **2**. The sample was then heated at 80 °C for 72 h. $^1H$ and $^{13}C\{^1H\}$ NMR spectra of the sample were identical with those of authentic samples of **2**.

**[$NBu^n_4$][Os(N){$O_2CCH(NHCOCH_3)CH_2S$}$_2$] (3).** A solution of 0.034 g (0.20 mmol) of *N*-acetyl-L-cysteine and 56 μL of $Et_3N$ (0.40 mmol) in 10 mL of $CH_2Cl_2$ was added dropwise with magnetic stirring to a cold (−30 °C) solution of 0.060 g (0.102 mmol) of [$NBu^n_4$][Os(N)$Cl_4$] in 30 mL of $CH_2Cl_2$. The solution turned from pink to bright yellow upon addition of the cysteine amine solution. The volume was concentrated in vacuo to 3 mL and filtered through Celite. Yellow needles of [$NBu^n_4$][Os(N){$O_2CCH(NHC(O)CH_3)CH_2S$}$_2$] and brown blocks of $Et_3NHCl$ were produced after slow vapor diffusion of diethyl ether into the reaction mixture. The crystals of **3** were obtained in 88% yield after manual separation from $Et_3NHCl$: mp 140–150 °C dec; $^1H$ NMR (500 MHz, $CDCl_3$, 18 °C) δ 6.84 (d, 2 H, $O_2CCH(NHC(O)CH_3)CH_2S$, $J$ = 5.8 Hz), 5.30 (s, 1 H, $CH_2Cl_2$), 4.79 (m, 2 H, $O_2CCH(NHC(O)CH_3)CH_2S$), 3.62 (dd, 2 H, $O_2CCH(NHC(O)CH_3)CH_2S$, $J$ = 3.65, 11.57 Hz), 3.26 (m, 8 H, $CH_2CH_2CH_2CH_3$), 2.82 (t, 2 H, $O_2CCH(NHC(O)CH_3)CH_2S$, $J$ = 11.8 Hz), 1.99 (s, 6 H, $O_2CCH(NHC(O)CH_3)CH_2S$), 1.60 (m, 8 H, $CH_2CH_2CH_2CH_3$), 1.32 (m, 8 H, $CH_2CH_2CH_2CH_3$), 0.98 (t, 12 H, $CH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, 18 °C) δ 13.64 ($CH_2CH_2CH_2CH_3$), 19.72 ($CH_2CH_2CH_2CH_3$), 23.31 ($O_2CCH(NHC(O)CH_3)CH_2S$), 23.90 ($CH_2CH_2CH_2CH_3$), 30.61 ($O_2CCH(NHC(O)CH_3)CH_2S$), 54.88 ($O_2CCH(NHC(O)CH_3)CH_2S$), 59.92 ($CH_2CH_2CH_2CH_3$), 169.14 (C=O), 177.80 (NHC=O); IR (KBr, $cm^{-1}$) 3355 ($\nu_{N-H}$), 2961, 2873, 1654 ($\nu_{C=O}$), 1559, 1508, 1458, 1373, 1201, 1084 ($\nu_{NO_3}$). Anal. Calcd for $OsC_{26}H_{50}O_6N_4S_2 \cdot 0.5CH_2Cl_2$: C, 39.22; H, 6.33; N, 6.90. Found: C, 39.31; H, 6.52; N, 6.91.

**$HOC(O)CH_2CH_2SCH(C_6H_5)_2$.** 3-Mercaptopropionic acid (5 mL, 0.057 mol) was added by syringe to a solution of benzhydrol (10.57 g, 0.057 mol) in 20 mL of trifluoroacetic acid. The solution was mixed well and allowed to stand for 15 min with occasional stirring. It was then cooled to −30 °C and the crystalline product collected by vacuum filtration. The crystals were dissolved in $CH_2Cl_2$, which was then washed with water until the washings were neutral to litmus. The $CH_2Cl_2$ was then removed in vacuo to give a white crystalline solid. This was recrystallized from diethyl ether to give $HO_2CCH_2CH_2SCHPh_2$ (14.83 g, 95%): mp 88.5–90 °C. Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92. Found: C, 70.64; H, 5.92.

**$H_2NC(O)CH_2CH_2SCH(C_6H_5)_2$.** $HOC(O)CH_2CH_2SCH(C_6H_5)_2$ (5.0 g, 0.018 mol) was added to 7.5 mL of oxalyl chloride in a 25-mL flask fitted with a condenser and a gas trap. A large amount of gas was produced as the solution was gently refluxed until gas evolution ceased. The solution was allowed to cool and then the excess oxalyl chloride was removed in vacuo to give a bright yellow, viscous oil. An ammonia solution was then prepared by bubbling anhydrous ammonia through 50 mL of $CH_2Cl_2$ at 0 °C. The acid chloride was then added to the ammonia solution. Following a vigorous reaction, the white solid that formed was removed by filtration through Celite. The $CH_2Cl_2$ was then removed from the filtrate in vacuo to give a white solid which was added with diethyl ether and collected by vacuum filtration. $H_2NC(O)CH_2CH_2SCH(C_6H_5)_2$ (3.99 g, 80%) was obtained: mp 82.5–83.5 °C. Anal. Calcd for $C_{16}H_{17}NOS$: C, 70.82; H, 6.31; N, 5.16. Found: C, 70.56, H, 6.25, N, 5.20.

**$H_2NC(O)CH_2CH_2SH$.** In a 100-mL round-bottom flask, 30 mL of $NH_3$ was condensed and stirred with a glass stirbar. A freshly cut sample of Na (0.17 g, 0.0074 mol) was added to the $NH_3$. $H_2NC(O)CH_2CH_2SCH(C_6H_5)_2$ (1 g, 0.0037 mol) was mixed with $NH_4Cl$ (0.40 g, 0.0074 mol) and this was added to the blue solution of $NH_3$–Na. The solution became colorless and white solid precipitated. The $NH_3$ was allowed to evaporate and 20 mL of $CH_2Cl_2$ was added to the white residue. The solution was filtered in vacuo and the solid filtercake was washed with water. This solid was then crystallized from $CH_3OH$ to give $H_2NC(O)CH_2CH_2SH$ (0.120 g, 31%) as a white, crystalline solid. Anal. Calcd for $C_6H_{12}O_2N_2S_2$: C, 34.60; H, 5.81; N, 13.45. Found: C, 34.23; H, 5.78; N, 13.21.

**[$NBu^n_4$][Os(N)($NHCOCH_2CH_2S$)$_2$] (4).** To a solution of 0.10 g (0.125 mmol) of [$NBu^n_4$][Os(N)($OSiMe_3$)$_4$] in 30 mL of $CH_2Cl_2$ was added 0.65 g (0.62 mmol) of 3-mercaptopropionamide. The solution turned from pink to bright yellow. It was stirred for 12 h and the concentrated in vacuo. The residue was chromatographed on silica gel and eluted with diethyl ether. Solvent was removed in vacuo from a yellow band to yield 0.067 g (82%) of a golden solid. $^1H$ NMR (300 MHz, $CD_3CN$) δ 6.25 (s, 1 H, NH), 3.05 (t, 8 H, $NCH_2CH_2CH_2CH_3$), 2.85 (m, 2 H, $CH_2$), 2.6 (m, 2 H, $CH_2$), 1.60 (m, 4 H, $NCH_2CH_2CH_2CH_3$), 1.32 (m, 4 H, $NCH_2CH_2CH_2CH_3$), 0.98 (t, 6 H, $NCH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CD_3CN$) δ 13.67 ($NCH_2CH_2CH_2CH_3$), 20.18 ($NCH_2CH_2CH_2CH_3$), 24.1 ($NHCOCH_2CH_2S$), 24.15 ($NCH_2CH_2CH_2CH_3$), 42.3 ($NHCOCH_2CH_2S$); IR (KBr, $cm^{-1}$) 1603 ($\nu_{C=O}$), 1381, 1268, 1171, 1085 ($\nu_{NO_3}$), 1021. Anal. Calcd for $OsC_{22}H_{46}O_2N_4S_2$: C, 40.47; H, 7.10; N, 8.58. Found: C, 40.76; H, 7.24; N, 8.34.

**[$NBu^n_4$][Ru(N)($CH_2SiMe_3$)$_2$($SCH_2CH_2CO_2$)] (5).** [$NBu^n_4$][Ru($CH_2SiMe_3$)$_4$] (50 mg, 0.07 mmol) was dissolved in 15 mL of diethyl ether and cooled to −30 °C. A solution of 7.5 mg (6.2 μL, 0.07 mmol) of 3-mercaptopropionic acid in 3 mL of diethyl ether was then added dropwise to the cold solution of [$NBu^n_4$][Ru(N)($CH_2SiMe_3$)$_4$]. The solution was slowly warmed to room temperature and stirred for 2 h. It was filtered through Celite, and the solvent was removed in vacuo from the filtrate to give a yellow oil. Orange needles of **5** (36 mg, 80%) formed slowly from a mixture of the oil and hexane: $^1H$ NMR ($CDCl_3$, 500 MHz, 20 °C) δ 3.17 (vt, 8 H, $NCH_2CH_2CH_2CH_3$), 2.93 (m, 2 H, $NHC(O)CH_2CH_2S$), 2.65 (m, 2 H, $NHC(O)CH_2CH_2S$), 1.56 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 1.4 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 0.97 (t, 12 H, $NCH_2CH_2CH_2CH_3$), 0.0 (s, 9 H, $CH_2Si(CH_3)_3$), −0.41 (s, 9 H, $CH_2Si(CH_3)_3$). $^{13}C$ NMR ($CDCl_3$, 125 MHz, 20 °C) δ 180.6 ($NHC(O)CH_2CH_2S$), 58.7 ($NCH_2CH_2CH_2CH_3$), 42.4 ($NHC(O)CH_2CH_2S$), 26.4 ($NHC(O)CH_2CH_2S$), 24.4 ($CH_2Si(CH_3)_3$), 23.9 ($NCH_2CH_2CH_2CH_3$), 19.7 ($NCH_2CH_2CH_2CH_3$), 13.6 ($NCH_2CH_2CH_2CH_3$), 9.9 ($CH_2Si(CH_3)_3$), 1.7 ($CH_2Si(CH_3)_3$), 1.0 ($CH_2Si(CH_3)_3$); IR (KBr, $cm^{-1}$) 1603 ($\nu_{C=O}$), 1076 ($\nu_{RuN}$), 1026, 934, 749, 718, 680. Anal. Calcd for $RuC_{27}H_{62}O_2N_2Si$: C, 50.98; H, 9.82; N, 4.40. Found: C, 51.31; H, 10.06; N, 4.59.

**[$NBu^n_4$][Ru(N)($CH_2SiMe_3$)$_2$[$SCH_2CH(NHCOCH_3)CO_2$]] (6).** *N*-acetyl-L-cysteine (0.023 g, 0.142 mmol) in 5 mL of 1:1 $CH_2Cl_2$–diethyl ether was added dropwise to [$NBu^n_4$][Ru(N)($CH_2SiMe_3$)$_4$] (0.100 g, 0.142 mmol) in diethyl ether at −30 °C. The solution was warmed to room temperature over a 30-min period. Solvent was removed in vacuo to give a yellow-brown oil. The oil was chromatographed on neutral silica gel and eluted with acetonitrile. Solvent was removed from a yellow band to give **6** (0.090 g, 91%) as a yellow-orange oil: $^1H$ NMR ($C_6D_6$, 500 MHz, 20 °C) δ 7.47 (d, 1 H, $NHCOCH_3$, $J$ = 5 Hz), 5.06 (m, 1 H, $CH_2CH(NHCOCH_3)CO_2$), 3.56 (dd, 1 H, $CH_2CH(NHCOCH_3)CO_2$, $J$ = 4, 11 Hz), 2.80 (dd, 1 H, $CH_2CH(NHCOCH_3)CO_2$, $J$ = 11, 4 Hz), 1.58 (s, 3 H, $NHCOCH_3$), 1.50 (dd, 2 H, $RuCH_2SiMe_3$), 0.47 (s, 9 H, $RuCH_2SiCH_3$), 0.35 (s, 9 H, $RuCH_2SiCH_3$); $^{13}C$ NMR ($C_6D_6$, 125 MHz, 20 °C) δ 177.3 ($CH(NHCOCH_3)C(O)O$), 168.5 ($CH(NHCOCH_3)C(O)O$), 58.8 ($CH_2CH(NHCOCH_3)CO_2$), 29.6 ($NHCOCH_3$), 25.6 ($SCH_2CH(NHCOCH_3)CO$), 13.8 ($RuCH_2SiMe_3$), 2.0 ($RuCH_2SiCH_3$), 1.93 ($RuCH_2SiCH_3$); IR (KBr, $cm^{-1}$) 2962, 1665 ($\nu_{C=O}$), 1626 ($\nu_{C=O}$), 1489, 1381, 1273, 1240, 1076 ($\nu_{RuN}$), 850, 830. Anal. Calcd for $RuC_{29}H_{62}O_4N_4$: C, 50.52; H, 9.45; N, 6.06. Found: C, 50.13; H, 9.58; N, 5.95.

**[$PPh_4$][Ru(N)($CH_2SiMe_3$)$_2$[$SCH_2CH(NHCOCH_3)CO_2$]] (6b)** was prepared as above from *N*-acetyl-L-cysteine and [$PPh_4$][Ru(N)($CH_2SiMe_3$)$_4$]: $^1H$ NMR ($CDCl_3$, 500 MHz, 18 °C) δ 7.89 (m, 4 H, *p*-$(C_6H_5)_4P$), 7.75 (m, 8 H, *o*-$(C_6H_5)_4P$), 7.57 (m, 8 H, *m*-$(C_6H_5)_4P$), 7.04 (d, 1 H, $NHC(O)CH_3$, $J$ = 5 Hz), 4.65 (m, 1 H, $OC(O)CH(NHC(O)CH_3)CH_2S$), 3.22 (dd, 1 H, $OC(O)CH(NHC(O)CH_3)CH_2S$, $J$ = 11, 4 Hz), 2.35 (dd, 1 H, $OC(O)CH(NHC(O)CH_3)CH_2S$, $J$ = 11, 4 Hz), 1.88 (s, 3 H, $NHC(O)CH_3$), 1.60 (d, 1 H, $CH_2Si(CH_3)_3$, $J$ = 10 Hz), 1.48 (d, 1 H, $CH_2Si(CH_3)_3$, $J$ = 11 Hz), 1.21 (d, 1 H, $CH_2Si(CH_3)_3$, $J$ = 11 Hz), 0.99 (d, 1 H, $CH_2Si(CH_3)_3$, $J$ = 10 Hz), 0.01 (s, 1 H, $CH_2Si(CH_3)_3$), −0.13 (s, 1 H, $CH_2Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 18 °C) δ 177.9 ($OC(O)CH(NHC(O)CH_3)CH_2S$), 168.4 ($OC(O)CH(NHC(O)CH_3)CH_2S$), 135.9 (*p*-$(C_6H_5)_4P$), 134.4 (*o*-$(C_6H_5)_4P$), 138.8 (*m*-$(C_6H_5)_4P$), 117.5 (d, *ipso*-$(C_6H_5)_4P$), 58.0 ($OC(O)CH(NHC(O)CH_3)CH_2S$), 28.9 ($OC(O)CH(NHC(O)CH_3)CH_2S$), 25.1 ($CH_2Si(CH_3)_3$), 23.6 ($OC(O)CH(NHC(O)CH_3)CH_2S$), 10.2 ($CH_2Si(CH_3)_3$), 1.44 ($CH_2Si(CH_3)_3$), 1.14 ($CH_2Si(CH_3)_3$).

**[$NBu^n_4$][Ru(N)($HNC(O)CH_2CH_2S$)$_2$] (7).** Excess 3-mercaptopropionamide was added to [$NBu^n_4$][Ru(N)($OSiMe_3$)$_4$] (0.100 g, 0.18 mmol) in 10 mL of $CH_2Cl_2$ at −30 °C. The mixture was warmed to room temperature and allowed to stir for 5 min. The color of the solution changed from purple to yellow-brown and the excess solid became dark brown. This was filtered through Celite to give a yellow-brown solution that was concentrated to a few milliliters in vacuo. The solution was chromatographed on silica gel with acetonitrile as the elutant. The first band off the column was collected as a bright yellow solution. The acetonitrile was removed in vacuo and the residue was taken up in $CH_2Cl_2$, filtered through Celite, and then evaporated to dryness. [$NBu^n_4$][Ru(N)($HNC(O)CH_2CH_2S$)$_2$] (0.036 g, 40%) was obtained as a bright yellow solid: $^1H$ NMR ($CDCl_3$, 500 MHz, 18 °C) δ 7.6 (s, 1

H, RuNHNC(O)), 3.15 (vt, 8 H, $NCH_2CH_2CH_2CH_3$), 2.90 (m, 4 H, $NHC(O)CH_2CH_2S$), 2.70 (m, 4 H, $NHC(O)CH_2CH_2S$), 1.62 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 1.45 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 1.0 (t, 12 H, $NCH_2CH_2CH_2CH_3$); $^{13}C$ NMR ($CDCl_3$, 125 MHz, 18 °C) δ 180.5 (RuNHC(O)), 58.7 ($NCH_2CH_2CH_2CH_3$), 42.3 ($NHC(O)CH_2CH_2S$), 26.4 ($NHC(O)CH_2CH_2S$), 23.9 ($NCH_2CH_2CH_2CH_3$), 19.7 ($NCH_2CH_2CH_2CH_3$), 13.6 ($NCH_2CH_2CH_2CH_3$); IR (KBr, $cm^{-1}$) 3314 ($\nu_{N-H}$), 2957, 2872, 1603 ($\nu_{CO}$), 1368, 1269, 1173, 1094 ($\nu_{RuN}$) 1048. Anal. Calcd for $RuC_{22}H_{46}O_2N_3$: C, 46.87; H, 8.12; N, 9.94. Found: C, 47.21; H, 8.30; N, 9.80.

**$[PPh_4][Ru(N)(HNC(O)CH_2CH_2S)_2]$ (7b)** was prepared as above from 3-mercaptopropionamide and $[PPh_4][Ru(N)(OSiMe_3)_4]$: $^1H$ NMR ($CDCl_3$, 500 MHz, 18 °C) δ 7.90 (m, 4 H, $p$-$(C_6H_5)_4P$), 7.76 (m, 8 H, $o$-$(C_6H_5)_4P$), 7.58 (m, 8 H, $m$-$(C_6H_5)_4P$), 5.82 (s, 1 H, $NHC(O)CH_2CH_2S$), 3.03 (m, 1 H, $NHC(O)CH_2CH_2S$), 2.85 (m, 2 H, $NHC(O)CH_2CH_2S$), 2.71 (m, 1 H, $NHC(O)CH_2CH_2S$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 18 °C) δ 180.7 ($OC(O)CH(NHC(O)CH_3)CH_2S$), 135.9 ($p$-$(C_6H_5)_4P$), 134.3 ($o$-$(C_6H_5)_4P$), 130.8 ($m$-$(C_6H_5)_4P$), 117.7 (d, $ipso$-$(C_6H_5)_4P$), 117.0 (d, $ipso$-$(C_6H_5)_4P$), 42.4 ($NHC(O)CH_2CH_2S$), 26.4 ($NHC(O)CH_2CH_2S$).

**Crystallization and Reduction of X-ray Diffraction Data.** Yellow crystals of **2** suitable for X-ray crystallographic analysis were grown by vapor diffusion of hexane into a THF solution and stored in THF-hexane under dinitrogen. The data crystal was mounted with oil (Paratone-N, Exxon) on an Enraf-Nonius CAD4 automated κ-axis diffractometer equipped with a graphite crystal monochromator (λ(Mo Kα) = 0.71073 Å). Data were collected at −75 °C and corrected for absorption, anomalous dispersion, Lorentz, and polarization effects. The structure was solved by direct methods.[33] The Os and N1 atoms were disordered in two positions with a relative site occupancy 0.922 (2); a common variable was refined for the disordered Os-N distance.

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Yellow crystals of **3** suitable for X-ray crystallographic analysis were grown by vapor diffusion of diethyl ether into a $CH_2Cl_2$ solution and stored in diethyl ether under dinitrogen. The data crystal was mounted with epoxy on an Enraf-Nonius CAD4 automated κ-axis diffractometer equipped with a graphite crystal monochromator (λ(Mo Kα) = 0.71073 Å). Data were collected at −75 °C and corrected for absorption, anomalous dispersion, Lorentz, and polarization effects. The mosaic spread was broad; typical ω-scan width at half-maximum was 0.5°. The structure was solved by Patterson methods.[30] Cation carbon atom C34 was disordered in two positions with relative site occupany 0.058 (5); amine hydrogen atoms did not surface in the final difference Fourier map.

Yellow crystals of **7b** suitable for X-ray crystallographic analysis were grown by slow crystallization from diethyl ether-hexane. The data crystal was mounted with epoxy on a Syntex $P2_1$ four-circle diffractometer equipped with Crystal Logic automation and a graphite crystal monochromator (λ(Mo Kα) = 0.71073 Å). Data were collected at 26 °C and the structure was solved by Patterson methods.[30] Positions for hydrogen atoms HN1 and HN2 were located and refined. Crystal and experimental data for all structures are summarized in the supplementary material.

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**Supplementary Material Available:** Tables of crystal and experimental data, atomic coordinates, thermal parameters, and selected distances and angles for **2**, **3**, and **7b** (18 pages); listings of observed and calculated structure factors (59 pages). Ordering information is given on any current masthead page.

# Enantioselective Esterifications of Unsaturated Alcohols Mediated by a Lipase Prepared from *Pseudomonas* sp.

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**Abstract:** Competition experiments and measurements of enantioselectivities were used to develop a simple active-site model (Figure 1) for resolutions of β-hydroxy-α-methylene carbonyl compounds III via acyl transfers mediated by lipase from *Pseudomonas* sp. (AK). Further experiments were used to test and refine this model with respect to resolutions of allylic, propargylic, homopropargylic, and other alcohols (Tables I-IV, respectively). The model proved extremely reliable for predicting the sense of the asymmetric induction, and the combined data collected in this paper give an indication of what structural features of the substrates can be correlated with high enantioselectivities in these resolutions. Furthermore, the results account for the conspicuous reversal of enantioselectivity previously observed in resolutions of γ-hydroxy-α,β-unsaturated esters **35**. Kinetic resolutions of two substrates (allenol **14** and dienol **9**) via asymmetric epoxidations were performed for comparison with the methodology presented in this paper.

Three relatively recent developments have vastly expanded the scope of biocatalytic resolutions in organic chemistry: (i) the realization that enzymes can be used in organic solvents,[1-7] (ii) the emergence of enol esters[8-12] and similar reagents[13] for essentially irreversible transfer of carboxylates, and (iii) commercial availability of a range of lipase preparations at low cost. Consequently, many chiral alcohols can be conveniently resolved via "enantioselective esterifications" wherein an enzyme mediates acyl transfer to enantiomers of a given alcohol at different rates.

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