is very similar, though the present approach involving diagonalization of the d^5 ligand field matrix yields estimates of the splitting of the $^2T_{2g}$ ground state which are ~15–25% larger than those derived by using the formulas of Taylor.

The orientations of the **g** tensors calculated for the porphyrin complexes are in excellent agreement with those observed experimentally. The largest g value was found to be parallel to the C_2 axis of each complex (the Fe–N(imidazole) bond directions). The other principal g axes are rotated away from the Fe–N(porphyrin) bond vectors, and the calculated rotation angles (23° for $[FeTPP(tMU)_2]SbF_6$ and 26° (A), 11° (B) for $[FeTPP(cMU)_2]SbF_6$) agree well with those observed experimentally (22° and 29° (A), 15° (B), respectively). Here, the rotation angle refers to the smallest g value, and rotation occurs in the direction opposite to that of the plane of the imidazole ligand (Figure 4c). It has been pointed out[2,21] that, in complexes such as these, the orientation of the **g** tensor will be dominated by the π-interactions with the amine ligands. The unpaired electron density is likely to be concentrated in the orbital of π-symmetry normal to the plane of the axial ligands. For the coordinate system shown in Figure 4c, the ground state will be of ^2B_g symmetry and will consist largely of a linear combination of the d_{xz} and d_{yz} orbitals. The rotation of the principal g axes away from the Fe–N bond directions is caused largely by coupling with the low-lying ^2A_g state, in which the unpaired electron occupies the d_{xy} orbital.[2,21]

For $[Fe(diammac)]^{3+}$, the dominant distortion from octahedral symmetry is due to the angular distortion of the terminal amine groups, and a simplistic interpretation might infer that, for the coordinate system shown in Figure 4a, the unpaired density should occupy the d_{xy} orbital. This would imply that the principle axis of the approximately axially symmetric **g** tensor, g_1, should lie along the **z** axis of the complex. Instead, g_1 approximately bisects the molecular **x** and **y** axes. In the C_{2h} point group of the complex, d_{xy}, $d_{x^2-y^2}$, and d_{z^2} all belong to the A_g representation, and it seems likely that the unpaired electron occupies an orbital composed of a mixture of these d functions, having lobes approximately normal to the g_1 principal axis. In both $[Fe(diammac)]^{3+}$ and $[Fe(o\text{-}phen)_3]^{3+}$, the deviation of the ligand field from octahedral symmetry is largely caused by angular distortions, and the orientation of the **g** tensors of the two complexes is remarkably similar when considered in this light. In $[Fe(o\text{-}phen)_3]^{3+}$, the deviation is due to the "bite" of each chelate ring being less than 90°, and the lowest g value is directed away from the three acute NFeN angles (Figure 4b). In just the same way, the lowest g value of $[Fe(diammac)]^{3+}$ is directed away from the two acute NFeN angles in this complex (Figure 4a).

Conclusions

It has been found that the rhombic **g** tensors measured for the two $[Fe(diammac)]^{3+}$ complexes present in $[Fe(diammac)](ClO_4)_3$ may be interpreted satisfactorily by using the angular overlap model. This model has also been applied successfully to the interpretation of the **g** tensors reported for iron(III) *o*-phenanthroline and porphyrin complexes. The orientation of the **g** tensor has been related to the way in which the ligand field deviates from octahedral symmetry in each complex. As expected, the **g** tensor in each case conforms to the point group symmetry of the complex. However, the relationship of the electronic structure to the molecular geometry of $[Fe(diammac)]^{3+}$, of C_{2h} symmetry, seems more closely analogous to that of $[Fe(o\text{-}phen)_3]^{3+}$, of D_3 symmetry, than to the porphyrin complexes which also belong to the C_{2h} point group.

Because the angular overlap model relates the **g** tensor directly to the molecular geometry and metal–ligand bonding parameters, both features of interest to nontheoretical chemists, it should provide a particularly useful method of interpreting the **g** tensors of biologically important molecules. Low-spin iron(III) complexes of biological significance have been the subject of numerous EPR investigations, and we are currently applying the model to the interpretation of the **g** tensors reported for a range of molecules of this kind.

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Cysteine Complexes of Oxoruthenium(VI): Synthesis and Characterization of $Ru(O)_2L_2\{SCH_2CHRC(O)O\}$ (L = py, 1/2 bpy; R = H, NHCHO, NHCOMe)

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Introduction

In the biosynthesis of isopenicillin N, it has been proposed that coordination of α-aminoadipoyl-L-cysteinyl-D-valine to an oxidized (ferryl) iron center occurs through the cysteinyl sulfur and the valine nitrogen.[1] The active site of this metalloenzyme, isopenicillin N synthetase (IPNS), has been studied spectroscopically by several groups who found that the iron center in the reduced enzyme is non-heme and is coordinated to histidine, water, and a cysteine residue.[2]

Transition-metal complexes of cysteine(2−) derivatives possessing monodentate coordination of the ligand through sulfur,[3] bidentate coordination through sulfur and nitrogen,[4] or tridentate coordination with sulfur, nitrogen, and oxygen atoms[5] have been previously prepared. Other species are insoluble polymers, presumably with bridging cysteine ligands.[6]

As a part of our efforts to model the active site of isopenicillin N synthetase, we have prepared high-oxidation-state complexes

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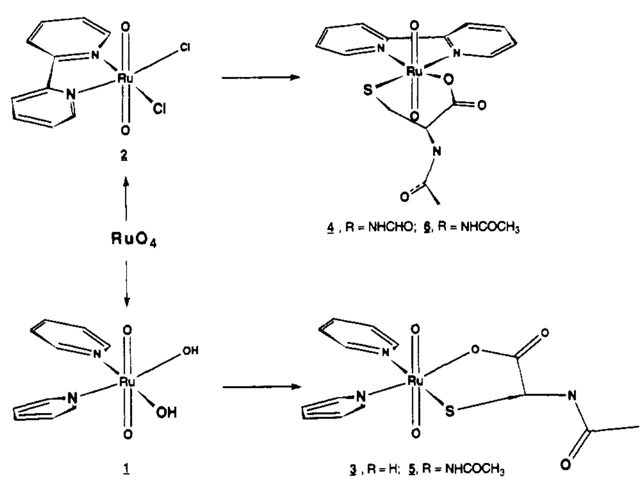
Scheme I



of the iron-triad metals with cysteine(2−) and related ligands. Because oxo complexes of iron in high oxidation states (+4 to +6) are unstable in the presence of easily oxidized organic molecules, we have substituted ruthenium for iron. Here we report the synthesis and characterization of four *trans*-dioxoruthenium(VI) complexes containing bidentate cysteinate-*S*,*O* or 3-mercaptopropionate-*S*,*O* ligands.

Results and Discussion

The *trans*-dioxoruthenium(VI) pyridine and bipyridine complexes $Ru(O)_2(OH)_2(py)_2$ (**1**) and $Ru(O)_2Cl_2(bpy)$ (**2**) can be readily prepared from ruthenium tetraoxide.[7] Addition of 1 equiv of 3-mercaptopropionic acid, *N*-formylcysteine, or *N*-acetylcysteine to either **1** or **2** in a 1:1 mixture of THF/CH_2Cl_2 at −78 °C or in DMF at room temperature produces the complexes $Ru(O)_2(py)_2\{SCH_2CH_2C(O)O\}$ (**3**), $Ru(O)_2(bpy)\{SCH_2CH(NCHO)C(O)O\}$ (**4**), $Ru(O)_2(py)_2(SCH_2CH(NHCOMe)C(O)O\}$ (**5**), and $Ru(O)(bpy)\{SCH_2CH(NHCOMe)C(O)O\}$ (**6**) in yields ranging from 60 to 87% (Scheme I). All are thermally stable amber or green microcrystalline solids which are soluble in polar organic solvents. Solvents used to recrystallize these complexes are frequently trapped in the crystal lattice.

IR spectroscopy shows that both the thiol and the carboxylic acid groups have been deprotonated. The S–H stretch, normally found between 2400 and 2600 cm^{-1}, and the broad O–H stretch, normally found between 3400 and 3200 cm^{-1}, are absent in the IR spectra of compounds **3**–**6**. The shift to lower energy of the asymmetric carboxyl stretch in the IR spectrum of each compound from that of 3-mercaptopropionic acid (1710 cm^{-1}) or the protected cysteines (1717 cm^{-1}) also indicates that the carboxylate oxygen coordinates to the metal.[4,6,8] The symmetric C–O stretch is obscured by bands due to the ancillary pyridine or bipyridine ligands. A trans arrangement of the oxo ligands is consistent with the infrared data for these complexes. Bands occur near 800 cm^{-1} in the IR spectra of compounds **3** and **5** and at 835 and 833 cm^{-1} in the IR spectra of **4** and **6**, respectively. These bands are similar to those in the starting materials, **1** and **2**, which have previously been assigned to O=Ru=O.[9] Similar *trans*-dioxoruthenium compounds whose structures have been determined by X-ray crystallography have a O=Ru=O stretching vibration between 800 and 850 cm^{-1}.[10] The stability of the *trans*-dioxo configuration for d^2 metals has been well established.[10,11]

The ^{1}H and ^{13}C NMR spectra of compounds **3**–**6** reveal that these complexes are diamagnetic. The spectra also provide information on the mode of coordination of the ligands to the ruthenium center. Resonances associated with the thiol and acid protons of the free ligands are absent from the ^{1}H NMR spectrum of each compound. The chemical shift differences between the two sets of methylene protons of **3** and the methylene and methyne protons of **4**–**6** increase upon coordination. The NMR data for these complexes are similar to those of $[NBu^n_4][Os(N)(SCH_2CH_2CO_2)_2]$ and $[NBu^n_4][Os(N)\{SCH_2CH(NHCOCH_3)CO_2\}_2]$, which have been shown by single-crystal X-ray diffraction studies to contain bidentate mercaptopropionate and *N*-acetylcysteinate(2−) ligands.[12]

The electronic properties of compounds **3**, **5**, and **6** were investigated by cyclic voltammetry and by UV–visible spectroscopy. Electrochemical experiments were performed in neutral water by using a Ag/AgCl reference electrode and a glassy carbon working electrode. Each solution was 0.1 M in $NaClO_4$ and 0.01 M in analyte. All potentials are expressed versus SCE. Cyclic voltammograms of complexes **3**, **5**, and **6** each show three reduction waves between +1000 and −700 mV. There are no oxidation waves at potentials up to 1300 mV. The first reduction occurs at 681 mV in **5**, at 631 mV in **6**, and at 551 mv in **3**. Each is a reversible reduction with approximately equal anodic and cathodic currents. A plot of $E_{pa} - E_{pc}$ vs scan rate gives an intercept near 59 mV in each case. The other reduction waves occur close to potentials of 211 and −319 mV in **3**, **5**, and **6** and are irreversible. Similar electrochemical behavior was also noted by Griffith and co-workers for a series of *trans*-dioxoruthenium(VI) pyridine complexes.[13]

Electronic spectra for complexes **3**, **5**, and **6** in DMSO or DMF are very similar to each other and to those of previously reported *trans*-dioxoruthenium pyridine complexes.[13,14] The UV–visible spectrum of each complex **3**, **5**, and **6** has an intense band near λ_{max} 260 nm and weaker bands near 400, 600, and 650 nm. In addition, the spectra of **3** and **5** also contain a band at 308 and 336 nm respectively. Bands reported by Che and Griffith near λ_{max} 200 nm are obscured by solvent in our spectra. The bands near 260 nm have been assigned to pyridine–metal charge-transfer transitions. The bands near 400 nm have been previously assigned to the *trans*-dioxo unit and provide further evidence of the trans disposition of the oxo ligands in these complexes.

Conclusion

We have synthesized a number of ruthenium(VI) complexes containing cysteinate(2−) and related ligands. Spectroscopic characterization shows that cysteine and mercaptopropionic acid bind in a bidentate fashion through sulfur and oxygen. Given the ease of oxidation of cysteine and related molecules, and the fact that ruthenium(VI) complexes are known to act as oxidants toward some organic molecules,[13] it is surprising that neither electron transfer nor oxo transfer between the ruthenium center and the thiolato ligand occurs in these complexes. The reaction chemistry of these compounds is currently under investigation.

Experimental Section

All operations were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques unless otherwise stated. Methylene chloride was distilled under nitrogen from CaH_2, while THF was distilled under nitrogen from Na/benzophenone. Dimethyl-d_6 sulfoxide (Aldrich), *N*-acetyl-L-cysteine (Aldrich), 3-mercaptopropionic acid (Aldrich), zinc dust (Mallinckrodt), formic acid (Aldrich), acetic anhydride (Aldrich), BaO (Aldrich), $NaClO_4$ (Mallinckrodt), and L-cystine (Aldrich) were used without further purification. *N*-Formyl-L-cysteine was prepared according to Zervas.[15]

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Dimethylformamide was distilled from KOH and then from BaO and stored over 4-Å molecular sieves prior to use in electrochemical experiments.

NMR spectra were obtained on either a Varian XL-200, a Nicolet NT-360, or a GE GN-500 spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1600 series FTIR instrument. Electrochemical experiments were performed on a BAS 100 electrochemical analyzer with glassy carbon working and platinum auxiliary electrodes and a Ag/AgCl reference electrode. Electrochemical solutions were approximately 0.1 M in electrolyte and 0.01 M in analyte. Ultraviolet and visible spectra were recorded on a Hewlett Packard Model 8452 diode-array spectrophotometer.

$Ru(O)_2(C_5H_5N)_2(C_3H_4O_2S)$ (3). A solution of **1** (0.055 g, 0.17 mmol) in 25 mL of CH_2Cl_2 was cooled to −78 °C. A solution of 3-mercaptopropionic acid (16 μL, 0.18 mmol) in 10 mL of CH_2Cl_2 was added dropwise to the $Ru(O)_2(OH)_2(C_5H_5N)_2$. The reaction mixture was slowly warmed to room temperature with magnetic stirring. A light green solid precipitated. This solid was collected by filtration, redissolved in pyridine, and precipitated with diethyl ether. The residue was dried under vacuum to give 0.040 g (60%) of the solvated product $Ru(O)_2(C_5H_5N)_2(C_3H_4O_2S)\cdot 0.25C_5H_5N$. IR (KBr pellet, cm^{-1}): 802 (RuO_2), 1657 (CO). ^1H NMR (CD_3CN, 360 MHz, 18 °C): δ 7.1–9.0 (m, 12.5 H, C_5H_5N), 2.88 (t, *J* = 7.0 Hz, 2 H, CH_2), 2.66 (t, *J* = 7.0 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 90 MHz, 35 °C): δ 172.6 (CO), 149.5 (py), 136.0 (py), 123.8 (py), 33.9 (CH_2), 33.3 (CH_2). UV–vis (DMF, 0.0014 M in analyte, nm): λ 266 (ε = 5333), 308 (4180), 420 (2600), 580 (2220), 636 (3390). Anal. Calcd for $RuC_{13}H_{14}N_2O_4S\cdot 0.25C_5H_5N$: C, 41.23; H, 3.70; N, 7.59. Found: C, 41.41; H, 3.94; N, 7.52.

$Ru(O)_2(C_5H_4N)_2(C_4H_5NO_3S)$ (4). The compound was synthesized according to the method used for **3** in 69% yield from **2** and *N*-formyl-L-cysteine. The methylene chloride solvate $Ru(O)_2(C_5H_5N)_2(C_4H_5NO_3S)\cdot CH_2Cl_2$ was obtained. IR (KBr pellet, cm^{-1}): 835 (RuO_2), 1600 (CO), 1650 (C=O), 3360 (NH). ^1H NMR ($(CD_3)_2SO$, 360 MHz, 18.4 °C): δ 8.10 (s, 1 H, *H*CO), 7.6–9.4 (m, 8 H, bpy), 5.60 (s, 2 H, CH_2Cl_2), 3.15 (dd, *J* = 4.4, 13.7 Hz, 1 H, CH_2), 2.95 (dd, *J* = 8.8 Hz, 13.7 Hz, 1 H, CH_2), 4.57 (m, 1 H, C*H*). Anal. Calcd for $RuC_{14}H_{13}N_3O_5S\cdot CH_2Cl_2$: C, 34.56; H, 2.90; N, 8.06; Cl, 13.6. Found: C, 34.76; H, 3.14; N, 8.03; Cl, 13.53.

$Ru(O)_2(C_5H_5N)_2(C_5H_7NO_3S)$ (5). In a typical procedure, a solution of *N*-acetylcysteine (0.027 g, 0.16 mmol) in 5 mL of DMF was added dropwise over a period of 15–20 min to a solution of **1** (0.052 g, 0.16 mmol) in 35 mL of DMF and 5 mL of CH_2Cl_2. The reaction mixture was allowed to stir for an additional 1 h at room temperature. A dark green solid was precipitated by the addition of diethyl ether and was filtered out and dried under vacuum to give the product as a CH_2Cl_2/DMF solvate $Ru(O)_2(C_5H_5N)_2(C_5H_7NO_3S)\cdot CH_2Cl_2\cdot 2DMF$ in 70% yield. IR (KBr pellet, cm^{-1}): 3272 (NH), 1655 (CO), 1602 (CO), 800 (RuO_2). ^1H NMR ($(CD_3)_2SO$, 360 MHz, 30 °C): δ 8.25 (d, *J* = 7.7 Hz, 2 H, py), 7.90 (s, 2.5 H, C*H*O), 7.76 (t, *J* = 7.7 Hz, 2 H, py), 7.37 (t, *J* = 6 Hz, 2 H, py), 5.65 (s, 2 H, CH_2Cl_2), 4.45 (m, *J* = 4.3 Hz, 1 H, C*H*), 3.14 (dd, *J* = 4.6 Hz, 13.7 Hz, 1 H, CH_2), 2.87 (dd, *J* = 9.0 Hz, 13.5 Hz, 1 H, CH_2), 2.80 (s, 7.5 H, NCH_3), 2.65 (s, 7.5 H, NCH_3), 1.83 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 125.7 MHz, 30 °C): δ 171.9 (CO), 169.2 (CO), 149.4 (py), 136.0 (py), 123.7 (py), 57.0 (CH_2Cl_2), 51.7 (CH), 22.2 (CH_3). UV–vis (DMSO, 0.001 72 M in analyte, nm): λ 266 (ε 710), 336 (488), 388 (686), 658 (405). FABMS: *m/z* 453, $(M + H)^+$. Anal. Calcd for $RuC_{15}H_{17}N_3O_5S\cdot CH_2Cl_2\cdot 2DMF$: C, 38.66; H, 4.87; N, 10.25; Cl, 10.37. Found: C, 38.30; H, 4.63; N, 10.55; Cl, 10.53.

$Ru(O)_2(C_5H_4N)_2(C_5H_7NO_3S)$ (6). This compound was synthesized according to the method used for **5** from **2** and *N*-acetyl-L-cysteine. The product was isolated in 87% yield as the methylene chloride solvate $Ru(O)_2(C_5H_4N)_2(C_5H_7NO_3S)\cdot CH_2Cl_2$. IR (KBr pellet, cm^{-1}): 3267 (NH), 1666 (CO), 1600 (CO), 833 (RuO_2). ^1H NMR ($(CD_3)_2SO$, 360 MHz, 18.0 °C): δ 9.40 (d, 2 H, bpy), 8.50 (t, 2 H, bpy), 8.10 (d, 2 H, bpy), 7.60 (t, 2 H, bpy), 5.60 (s, 2.2 H, CH_2Cl_2), 4.48 (m, 1 H, C*H*), 3.11 (dd, *J* = 4.6 Hz, 14 Hz, 1 H, CH_2), 2.90 (dd, *J* = 9.0 Hz, 14 Hz, 1 H, CH_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 125.7 MHz, 30 °C): δ 172 (CO), 170 (CO), 159.8, 154.2, 137.3, 126.8, 123.4 (bpy), 57.0 (CH_2Cl_2), 52.0 (CH), 22.0 (CH_3). UV–vis (DMSO, 0.001 23 M in analyte, nm): λ 249 (ε 3090), 412 (1170), 586 (245), 666 (1.40). FABMS: *m/z* 451, $(M + H)^+$. Anal. Calcd for $Ru(C_{15}H_{15}N_3O_5S)\cdot CH_2Cl_2$: C, 35.56; H, 3.19; N, 7.73; Cl, 14.34. Found: C, 35.68; H, 3.22; N, 7.91; Cl, 14.33.

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Preparation of Novel Low-Coordinate Chloro and Azido P–N Compounds. Attempted Synthesis of Cyclodiphosphazenes

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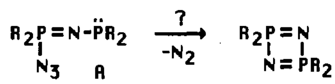
Introduction

Polyphosphazene chemistry is one of the most highly developed areas of phosphorus chemistry due to the large range of physical and chemical properties and to the wide industrial applications of these inorganic polymers. Various processes lead to the formation of such polymers, including, for example, the polymerization of cyclotriphosphazenes,[1] addition of phosphorus pentachloride to ammonium chloride,[2] polycondensation of *N*-(dichlorophosphoranyl)-*P*,*P*,*P*-trichloro-1λ^5-phosphazene,[3] and polycondensation of monomeric species such as $Me_3SiN{=}P(R_2)OCH_2CF_3$.[4] We have shown[5] that the photolysis of phosphane azides led to transient phosphonitriles (R_2PN), which are in fact the monomeric units of polyphosphazenes. Depending on the nature of the phosphorus substituents, the phosphonitriles may trimerize, oligomerize, and/or polymerize.[5d] In only one case have we been able to isolate and fully characterize a dimer, namely, the tetrakis(diisopropylamino)cyclodiphosphazene **1** (Scheme I).[5b,c] Since that report, only one other synthesis of **1** has been published.[6] It also involves the dimerization of a phosphinonitrene, but the precursor, the nitrilimine **2**, is not readily available, making this new route of no synthetic utility (Scheme I). All attempts to prepare other isolable dimers failed.[5d,7]

Although several hundred cyclotri-, cyclotetra-, and cyclopolyphosphazenes are known,[8] **1** is, surprisingly, the only example of a cyclodiphosphazene reported so far. This type of four-membered ring is of great importance, since it may shed new light on the question of equilibria among monomers, rings, and chains in phosphazenes. Such equilibria could be important in understanding the formation of commercial phosphazene resins. The development of the chemistry of cyclodiphosphazenes has been hindered by the lack of large-scale multigram syntheses of these compounds. Here we report our attempts to prepare new cyclodiphosphazenes via an intramolecular Staudinger reaction, starting from derivatives of type A.



Experimental Section

All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC80 or a Varian EM 360V spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as internal standard. ^{31}P NMR spectra were obtained on a Bruker AC80 spectrometer at 32.43 MHz. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 983 G spectrophotometer using a polystyrene film for calibration. Mass spectra were obtained on a Nermag R10-10H instrument. Photochemical reactions were performed in quartz tubes with a Rayonnet photochemical reactor.

Synthesis of [(Dichlorophosphanyl)imino]chlorobis(diisopropylamino)phosphorane (5). To a solution of 10 g (28.3 mmol) of [(trimethylsilyl)imino]chlorophosphorane **3** in dichloromethane (30 mL), maintained at −70 °C, was added dropwise a solution of 3.9 g (28.4

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