of the *n*-alkanol. Phenylalkanol intercalation compounds of $VO(p\text{-}CH_3OC_6H_4PO_3)\cdot 2H_2O$ are included by assuming the effective chain length of the phenyl group is equivalent to four methylene groups ($n = m + 4$). The data for methanol are omitted because single phases could not be produced, possibly due to some replacement of both water molecules in the dihydrate structure. The slopes of the lines in Figure 1 given the average layer spacing increase for each additional methylene group in the alkanol chain. The data for $n > 3$ give values of 1.03–1.09 Å/CH_2 unit. Since the maximum increase is 1.27 Å/CH_2 unit for an all trans alkyl chain, the data indicate a single layer of alkanol molecules between the vanadium phosphorus layers, with the alkanol chains inclined at an angle of 54–59°. The mean angle is close to that predicted (55°) for an all trans chain oriented so that the first bond is perpendicular to the layers. The alternation in spacing between odd and even values of *n*, which is most pronounced for phenyl alcohols, is also expected from this orientation. Monolayer formation and the stoichiometry of one alkanol molecule per formula unit suggest that in the organophosphonates the intercalant molecules are associated with specific sites on the interlayer surface. This behavior is in contrast to that observed in alcohol intercalation compounds of other layered solids, for example, $\alpha\text{-}VOSO_4$,[16] $Zr(HPO_4)_2$,[17] and clays,[18] which intercalate alkanols in bilayer arrangements.

The synthetic and intercalation chemistry of vanadyl organophosphonates is currently being extended to alkyl systems and also to organic substituents that introduce functional groups into the interlayer space, thereby enabling further chemical modification.

Registry No. $VO(C_6H_5PO_3)\cdot H_2O\cdot C_2H_5OH$, 92694-63-8; $VO(C_6H_5PO_3)\cdot 2H_2O$, 92669-39-1; $VO(p\text{-}CH_3OC_6H_4PO_3)\cdot H_2O\cdot C_2H_5OH$, 92669-40-4; $VO(p\text{-}CH_3OC_6H_4PO_3)\cdot 2H_2O$, 92669-41-5; $VO(p\text{-}C_6H_4C_6H_5PO_3)\cdot 2H_2O$, 92669-42-6.

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Received July 30, 1984

Models of Oxidized Heme Proteins. Preparation and Characterization of a *trans*-Dioxoruthenium(VI) Porphyrin Complex

Sir:

High-valent iron porphyrin complexes have been suggested for the oxidized states of the peroxidases,[1] and similar intermediates have been implicated in the oxygen-transfer reactions of cytochrome P-450[2] and the dioxygen reduction of cytochrome oxidase.[3] An understanding of the redox chemistry mediated by these enzymes has been hampered by the instability of these oxidized iron–heme intermediates and by the lack of simple chemical models for these reactive states. Synthetic examples of an oxoiron(IV) prophryin[4] and an oxoiron(IV) porphyrin cation radical[5] are now known; however, the thermal instability of each has prevented their isolation as pure solids. The periodic relationship of iron and ruthenium suggests that the latter could provide stable examples of oxidized metalloporphyrins. The oxidation of ruthenium(II) porphyrin complexes to μ-oxoruthenium(IV) dimers has recently been described,[6] and the reactivity of ruthenium(III) porphyrins for the catalytic oxygenation of hydrocarbons has been noted.[7] An oxoruthenium(IV) porphyrin cation radical was suggested as the reactive intermediate in this system. We describe here the isolation and characterization of the first *trans*-dioxoruthenium(VI) porphyrin complex.

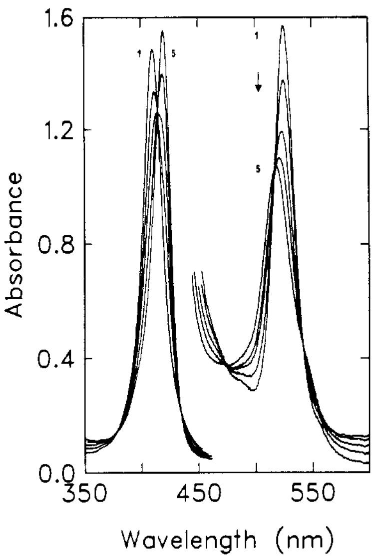

Figure 1. Visible spectral changes resulting from the titration of 6.7 × 10^{-6} M RuTMP(CO) in CH_2Cl_2 with increments of mCPBA. Equivalents of mCPBA present in solutions: (1) 0; (2) 0.5; (3) 1.0; (4) 1.5; (5) 1.9.

The addition of mCPBA to a methylene chloride solution of (5,10,15,20-tetramesitylporphyrinato)ruthenium(II) carbonyl[8] [RuTMP(CO) (**1**)] led to the appearance of a new species, **2**. The spectrophotometric titration of a 6.7 × 10^{-6} M solution of RuTMP(CO) with increments of mCPBA showed a smooth conversion of **1** to **2**, which was complete upon the addition of 2.0–2.5 equiv of mCPBA (Figure 1). The isosbestic points in the visible spectra at 380, 416, 478, 518, and 543 nm indicate that only **1** and **2** were present in appreciable quantities during this transformation. The identical reaction was observed when iodosylbenzene was used as the oxidant.

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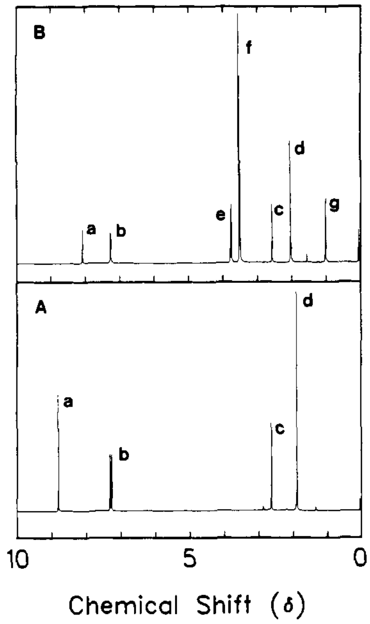
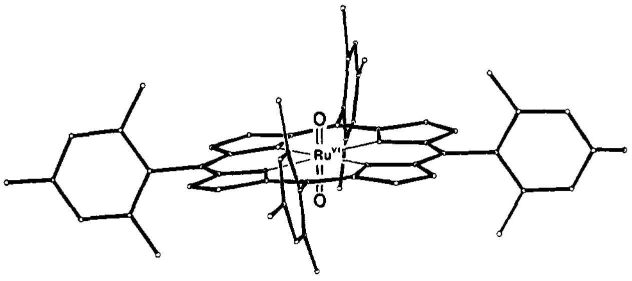


Figure 2. 360-MHz ^{1}H NMR spectra in $CDCl_3$ at room temperature: (A) $RuTMP(O)_2$ (**2**); (B) **2** + excess $P(OCH_3)_3$. Key: (a) pyrrole H; (b) meta H; (c) para methyl; (d) ortho methyl; (e) trimethyl phosphate; (f) trimethyl phosphite; (g) coordinated trimethyl phosphite.

Complex **2** was stable in air at room temperature for short periods and could be isolated in 60% yield after chromatography on basic alumina. Samples of **2** isolated in this way gave an elemental analysis in accord with the formulation $RuTMP(O)_2$.[9] Recrystallization from toluene/acetonitrile afforded a crystalline solid that was used for further spectroscopic characterization. Samples of pure **2** were surprisingly sensitive to decomposition apparently due to exposure to trace contaminants, particularly acids.

The ^{1}H NMR spectrum of **2** shows only sharp, unshifted resonances characteristic of the TMP ligand: δ 8.81 (pyrrole), 7.31 (meta H), 2.65 (para methyl), 1.91 (ortho methyl) (Figure 2A). These data indicate that **2** is diamagnetic. Further, since the ortho methyl and meta proton resonances appear as sharp singlets, a structure with D_{4h} symmetry is indicated. Accordingly, the ruthenium(IV) oxidation state can be ruled out for **2**. A monomeric ruthenium(IV) complex would be expected to have two unpaired electrons. A μ-oxo ruthenium(IV) dimer could not have such a symmetrical NMR spectrum, and the ortho methyl groups of the TMP ligand appear to preclude such a structure on steric grounds.

A *trans*-dioxoruthenium(VI) porphyrin structure is in accord with the NMR, the elemental composition of **2**, and the stoichiometry of the conversion of **1** to **2**. The electronic structure of such a species would be expected to be $(d_{xy})^2$. By contrast the d^0 electronic state of dioxomolybdenum(VI) porphyrins results in a cis geometry for the oxo ligands.[10]



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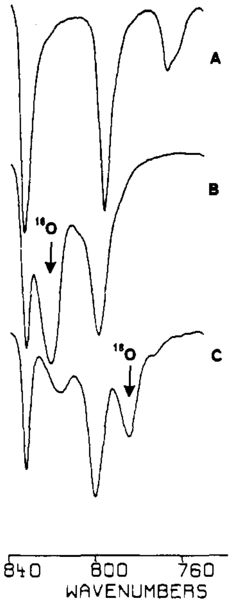

Figure 3. IR spectra (840–750 cm^{-1}) of **1** and **2** (KBr): (A) RuTMP(CO) (**1**); (B) **2** from reaction of **1** with mCPBA; (C) **2** from the reaction of **1** with $PhI^{18}O$.

The infrared spectrum of **2** shows a strong band at 821 cm^{-1} and no absorbance corresponding to the CO band which was observed for **1** at 1940 cm^{-1}. Samples of **2** prepared from ^{18}O-iodosylbenzene show a new band at 785 cm^{-1} (Figure 3) in good agreement with the 35-cm^{-1} shift predicted by a Hooke's law calculation for a harmonic linear O=Ru=O vibration. This assignment is in accord with analogous assignments for $OsOEP(O)_2$[11] at 825 cm^{-1} and several *trans*-dioxoruthenium complexes with simple ligands[12] (ca. 830 cm^{-1}). By contrast, *cis*-$MoTTP(O)_2$ exhibits two MoO_2 stretches.[10b]

That **2** contained two chemically available oxo ligands was demonstrated by its reaction with trimethyl phosphite. Thus, the addition of excess $P(OCH_3)_3$ to solutions of **2** in $CDCl_3$ at room temperature led to the appearance of a new porphyrin species, **3**, which was shown to be $Ru^{II}TMP[P(OCH_3)_3]_2$ by independent synthesis according to literature methods.[13] The ^{1}H NMR spectrum of this reaction mixture (Figure 2B) shows resonances for trimethyl phosphate (δ 3.78, J_{PH} = 11 Hz), unreacted trimethyl phosphite (δ 3.52, J_{PH} = 10.7 Hz), coordinated trimethyl phosphite, and the TMP ligand of **3**. Integration of these resonances indicated that 2 mol of $OP(OCH_3)_3$ had been produced for each mole of **3** and, accordingly, that the overall transformation had occurred with the stoichiometry indicated in eq 1. The transfer of oxo ligands from metalloporphyrins to phosphines and phosphites has also been reported for $Mo^{VI}TPP(O)_2$,[10c] $(L)Fe^{IV}TPP(O)$,[4b] and $Cr^{IV}TTP(O)$.[14]

The oxidation of $Ru^{II}TTP(CO)$ with mCPBA under conditions identical with those used to prepare **2** afforded two

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(9) Anal. Calcd for $RuTMP(O)_2$ (**2**, $C_{56}H_{52}N_4O_2Ru$): C, 73.58; H, 5.73; N, 6.13. Found: C, 72.90; H, 5.87; N, 6.08. UV (λ_{max}, nm $10^{-3}\epsilon$, M^{-1} cm^{-1}) (benzene): 330 (20), 400 sh (48), 422 (297), 516 (16), 540 sh (7.5).

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$$\underset{2}{Ru^{VI}TMP(O)_2} + 4P(OCH_3)_3 \rightarrow \underset{3}{Ru^{II}TMP[P(OCH_3)_3]_2} + 2OP(OCH_3)_3 \quad (1)$$

porphyrins, **4** and **5**, that lacked infrared bands between 700 and 900 cm^{-1} assignable to Ru=O. Further, **5** did not react with trimethyl phosphite at 25 °C. The ^1H NMR spectrum of **5** was completely consistent with the formulation $O[Ru^{IV}TMP(mCB)]_2$, and the conversion of **4** to **5** upon the addition of mCBA suggested $O[Ru^{IV}TMP(OH)]_2$ for **4**. Accordingly, the stability of **2** with respect to these dimers is dependent upon the steric hindrance of the ortho methyl groups of the mesityl substituents.[15]

The cyclic voltammetric behavior of **2** indicated that formal oxidation states higher than Ru(VI) are chemically available with this system. The cyclic voltammogram of **1** in methylene chloride (0.1 M tetrabutylammonium perchlorate) shows reversible potentials at 0.60 and 1.08 V vs. SCE. Similar results have been reported for RuTPP(CO) at slightly higher potentials.[16] By contrast, a single reversible oxidation wave was observed for **2** at 1.12 V. Electrolysis of **2** in a thin-layer spectroelectrochemical cell at 1.3 V generated a new species, **6**, with absorption maxima at 412 and 609 nm and a 60% decrease in absorbance of the Soret band relative to **2**. Applying a potential of 0.75 V regenerates **2** nearly quantitatively, implying that degradation of the porphyrin or loss of oxo ligands does not occur upon formation of **6**. The visible spectrum of **6** is similar to those of several Ru(II) porphyrin cation radical complexes,[17] especially with regard to the significant decrease in absorbance at the Soret band relative to the unoxidized complex. Hence, it is reasonable that the site of oxidation of **2** is the porphyrin rather than the metal and that **6** is best formulated as a porphyrin cation radical complex, $Ru^{VI}TMP(O)_2{}^+ClO_4{}^-$. The spectroscopic characterization of **6** and the reactivity of **2** and **6** in oxygen-transfer reactions are under study.

Acknowledgment. We thank Dow Chemical Co. for a fellowship for R.Q. Other aspects of this research were supported by the National Institutes of Health (Grant GM 25923). Michael Stern assisted with the spectroelectrochemical measurements.

Registry No. **1**, 92669-43-7; **2**, 92669-44-8; **3**, 92694-64-9; **4**, 92694-65-0; **5**, 92694-66-1; **6**, 92669-46-0; $Ru^{II}TTP(CO)$, 75888-64-1; $P(OCH_3)_3$, 121-45-9.

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(15) Visible spectral transients observed immediately upon addition of mCPBA to $Ru^{II}TTP(CO)$ indicated that a species analogous to **2** is formed prior to **4** and **5**.

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(18) Abbreviations: TPP, tetraphenylporphyrin; TTP, tetra-*p*-tolylporphyrin; TMP, tetramesitylporphyrin; mCPBA, *m*-chloroperoxybenzoic acid; mCBA, *m*-chlorobenzoic acid; mCB, *m*-chlorobenzoate; OEP, octaethylporphyrin.

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Received August 28, 1984

Articles

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Redirected Ligand-Field Analysis. 1. Ligand Fields of Coordination Voids and "Semicoordination" in Copper(II) Complexes

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Received November 14, 1983

The electronic d–d spectra of 11 complexes of copper(II) are analyzed within the angular-overlap model (AOM) formalism. Two analyses are reexaminations of tetrahedral $[CuCl_4]^{2-}$ and trigonal-bipyramidal $[CuCl_5]^{3-}$ ions in terms solely of traditional e_σ and e_π parameters taking normal values. The remaining nine studies demonstrate how e_σ values for the axial ligands, or lack thereof, in essentially tetragonal systems range from positive to negative as the axial interactions weaken. The significance of this variation and its relationship with variable equatorial AOM parameters in the complexes are discussed in terms of the new ligand-field formulation of the AOM. The concept of a "global overlay" upon the AOM definition of "local" chemical functionality in ligand-field theory is demonstrated. An incidental feature of the analyses is an evident irrelevance of ESR g values in these, and possibly other, copper(II) complexes.

Introduction

Although ligand-field theory did not begin or evolve within the mainstream chemical literature, that is where most attempts to exploit it are to be found. At the outset, therefore, it is right for us to emphasize that this subject is properly directed toward the formulation and clarification of concepts of chemical bonding and electron distribution in complexes. The reproduction of experimental ligand-field properties by quantum-mechanical models, which must always be done with care and technical skill, is merely a means toward an essentially chemical goal. If not, then however important or beautiful a study may be, it is surely not part of the chemical discipline. Too often in the past, research of this kind has purported to address chemical issues and its transparent failures to do so have engendered a rather widely held indifference to an "over-technical, irrelevant and passé" area of chemical endeavor.[1] Our own view now is that a new version of the angular-overlap model (AOM) provides the means by which ligand-field studies might be properly redirected. The formalism and theoretical structure of the approach have been

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