

and β -carbon signals in comparison to that in spin-admixed complexes (Table II).

Other physicochemical parameters of **1** and **2** are completely consistent with the ^1H and ^{13}C NMR data. ESR spectra of **1** and **2** as microcrystalline solids at both ambient temperature and 77 K or in frozen chloroform solution at 77 K are invariant, with a strong transition at $g_{\perp} = 4.2$ and a weak signal at $g_{\parallel} \approx 2$, values expected for $S = 3/2$ iron.^{2,19} Line shape is typical of complexes retaining axial symmetry.²⁰ Mössbauer spectra (Table III) of microcrystalline **1** and **2** at ambient temperatures are clearly indicative of $S = 3/2$ iron.⁵ The slight decrease in quadrupole splitting for **2** correlates with the downfield shift of the pyrrole proton resonance and supports interpretation of the ^1H NMR data as reflecting some $S = 5/2$ admixture in the 2 THF complex. Ambient-temperature solid-state moments of analytical samples of **1** and **2** were determined to be $\mu_{\text{eff}} = 4.6$ and $4.7 \mu_{\text{B}}$ respectively, based upon the molecular weights of the mono(chloroform) solvates. Because the influence of orientational effects and solvate on solid-state moments cannot be estimated,⁶ these results serve primarily to confirm that the magnetic properties of **1** and **2** are consistent with the intermediate-spin state for the complexes.

[TPP(2,4,6-OCH₃)₃]FeClO₄ is unique among (perchlorato)(tetraarylporphinato)iron(III) complexes described to date because it appears to be a true intermediate-spin ferric complex at ambient temperature both in the solid state and in chloroform solution. The physicochemical characteristics of this compound indicate that the stereochemistry around iron and the electron-withdrawing/-donating capability of peripheral substituents as well as axial ligand field strength may be critical determinants of spin state.

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Registry No. **1**, 90764-29-7; **2**, 90764-31-1; [TPP(2,4,6-OC₃H₃)₃]FeCl, 53470-05-6.

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Comment on Two Papers by R. H. Magnuson concerning Osmium(V) Compounds. Synthesis of $\text{SCl}_3[\text{OsCl}_6]$

Sir:

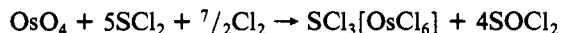
Magnuson just reported the synthesis of the OsCl_6^- ion by oxidation of OsCl_6^{2-} with PbO_2 in acetonitrile.¹ He characterized the OsCl_6^- ion by its spectral properties and, in a second paper together with Kim and Eriks, by the crystal structure determination of $\text{PPh}_4[\text{OsCl}_6]$.² In both papers the OsCl_6^- ion is claimed to be a new species, although it has been known since 1980 after we prepared $\text{AsPh}_4[\text{OsCl}_6]$ by the reaction of OsCl_5 with AsPh_4Cl in a $\text{C}_2\text{F}_3\text{Cl}_3$ suspension.³

Meanwhile, Preetz and Bruns described still another method of synthesis by chlorination of $\text{NEt}_4[\text{Os}(\text{CO})_4\text{Cl}_2]$ at 130°C .⁴ Infrared^{3,4} and resonance Raman⁴ as well as ultraviolet/visible⁴ spectral properties of the OsCl_6^- ion were reported.

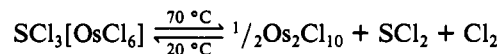
Investigation of osmium(V) chemistry has been substantially simplified by the facile synthesis of osmium pentachloride. Instead of the synthesis via OsF_6 ,⁵ $\text{Os}_2\text{Cl}_{10}$ can be easily and quantitatively prepared by the reaction of OsO_4 with SCl_2 .³ Accordingly, known osmium(V) compounds are no longer limited to those cited by Magnuson. A well-characterized osmium(V) complex is $\text{PPh}_4[\text{Cl}_5\text{OsNC}(\text{CCl}_3)\text{NCCl}(\text{CCl}_3)]\cdot\text{CH}_2\text{Cl}_2$,⁶ in which the Os-Cl bonds are found to be slightly longer than in $\text{PPh}_4[\text{OsCl}_6]$.²

The reported crystal structure of $\text{PPh}_4[\text{OsCl}_6]$ shows it to be isostructural with $\text{PPh}_4[\text{NbCl}_6]$,⁷ which is very closely related to the well-known and frequently encountered $\text{AsPh}_4[\text{RuNCl}_4]$ structure type, crystallizing in the space group $P4/n$.⁸ Packing conditions in PPh_4^+ and AsPh_4^+ salts have been thoroughly studied.⁸ In the specific case of $\text{PPh}_4[\text{NbCl}_6]$,⁷ exactly the same situation as in $\text{PPh}_4[\text{OsCl}_6]$ is found. In their structural paper,² Magnuson and co-workers wonder in a full column length why the atom Cl(2) exhibits an anomalous thermal vibration and why the OsCl_6^- ion deviates from perfect octahedral symmetry. Although they realize that the atom Cl(1) (trans to Cl(2)) has relatively short contact distances to phenyl hydrogen atoms whereas Cl(2) does not and that the intermolecular distance Cl(1)---Cl(2) is abnormally short, they do not draw the correct conclusion: there is no unusual thermal motion, but the OsCl_6^- ion is slightly disordered in the crystal in that only the atom Cl(1) is situated exactly on the crystallographic fourfold axis. The rest of the ion, most markedly atom Cl(2), is tilted away from this axis. This way, the intermolecular distance Cl(1)---Cl(2) is increased while in the structure determination an unusual thermal motion and a distortion from octahedral symmetry is feigned. This situation has already been analyzed in the case of $\text{PPh}_4[\text{NbCl}_6]$ and has been found similarly in other compounds such as $\text{AsPh}_4[\text{ReCl}_4(\text{NO})_2]$ ⁹ and $\text{AsPh}_4[\text{WScCl}_5]$.¹⁰ In $\text{AsPh}_4[\text{OsCl}_6]$, the IR spectrum shows that the OsCl_6^- ion cannot deviate considerably from octahedral symmetry.³

Additionally, we wish to report the preparation of another OsCl_6^- compound, which can be used as an excellent starting material to prepare other osmium(V) species. $\text{SCl}_3^+[\text{OsCl}_6^-]$ can be obtained in a simple reaction with quantitative yield by the reaction of OsO_4 with excess SCl_2 (which simultaneously acts as solvent) in the presence of chlorine at room temperature:



From this, $\text{Os}_2\text{Cl}_{10}$ can be obtained by thermal decomposition in vacuo with excellent yield:



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The reverse reaction takes place at room temperature, giving brown-red $\text{SCl}_3[\text{OsCl}_6]$ as a very hydrolysis-sensitive crystal powder. Anal. Calcd: Cl, 58.94; S, 5.92. Found: Cl, 58.33, S, 5.43.

The IR spectrum of $\text{SCl}_3[\text{OsCl}_6]$ exhibits strong absorption bands due to the SCl_3^+ ion (cm^{-1}): 494 vs. $\nu_{\text{as}} \text{SCl}_3$ (E); 469 s, $\nu_s \text{SCl}_3$ (A_1); 265 s, δSCl_3 (A_1). These values are comparable, although somewhat lower, with those in other SCl_3^+ compounds.¹¹ The F_{1u} stretching vibration of the OsCl_6^- ion

is observed as a strong band at 313 cm^{-1} . This value is lower than in other OsCl_6^- compounds, an effect that probably has to do with the electrostatic interaction between ions, as decreasing cation size goes parallel with decreasing frequency (cf. $\text{AsPh}_4[\text{OsCl}_6]$ (337 cm^{-1}),³ $\text{PPh}_4[\text{OsCl}_6]$ ($338, 330 \text{ sh cm}^{-1}$),¹ $\text{NEt}_4[\text{OsCl}_6]$ (325 cm^{-1}).⁴

Registry No. $\text{PPh}_4[\text{OsCl}_6]$, 86365-50-6; $\text{SCl}_3[\text{OsCl}_6]$, 91002-45-8.

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Articles

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Molybdenum(VI)-Dioxo Complexes with Sterically Bulky Ligands

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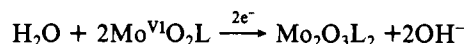
New molybdenum(VI)-dioxo complexes with a number of ligands having sterically bulky substituents have been synthesized. One-electron coulometric reduction of MoO_2LH_2 complexes ($\text{LH}_4 = N,N'$ -bis(2-hydroxy-3-*tert*-butylbenzyl)-1,2-diaminoethane (3-*t*-Bu-hbeH₄) and related ligands having 3-*tert*-butyl groups and N,N' -bis(2-ethyl-2-mercaptobutyl)-1,2-diaminoethane) in aprotic solvents gives stable Mo(V) monomers, while complexes without these ligand structures give Mo(V) oxo-bridged dimers. The X-ray structure of $\text{MoO}_2(3\text{-}t\text{-Bu-hbeH}_2)$ indicates the molecule has effective C_2 symmetry and suggests oxo-bridged dimer formation upon reduction is prevented by the 3-*tert*-butyl groups by steric hindrance. The room-temperature EPR spectra of the Mo(V) complexes exhibit coupling of 0.21–0.26 mT to two ¹⁴N nuclei, indicating the ligands likely have deprotonated amino groups. Chemical reduction of MoO_2LH_2 gives MoOLH_2 complexes which, upon one-electron coulometric oxidation, give Mo(V) complexes without ¹⁴N coupling to the Mo(V) EPR signal and with EPR parameters different from those of the complexes obtained by one-electron reduction of MoO_2LH_2 .

Introduction

Molybdenum is an essential component of a number of enzymes that catalyze two-electron redox processes.^{2,3} The molybdenum centers are thought to cycle between the VI, V, and IV oxidation states during catalysis, with the distribution of electrons between the molybdenum and other redox centers of the enzymes governed by their relative reduction potentials.^{2,4} The results of recent EXAFS⁵ and EPR⁶ investigations of sulfite oxidase and assimilatory nitrate reductase indicate the presence of two oxo ligands, two or three thiolate ligands, and, possibly, additional nitrogen, oxygen, or thioether ligands of molybdenum in the oxidized (Mo(VI)) state. Upon reduction (Mo(V/IV)), one oxo is lost; EPR evidence suggests it is converted to an OH^- ligand.^{5,6}

A large number of Mo(VI)-dioxo complexes are known, some of which have been proposed as models for the molybdenum centers of these enzymes.⁷⁻¹¹ Upon one-electron re-

duction, however, most Mo(VI)-dioxo complexes give EPR-silent, Mo(V) oxo-bridged dimers:¹²



In our search for more satisfactory models, we have synthesized a number of new Mo(VI)-dioxo complexes with sterically bulky ligands that inhibit the close approach of two Mo(V)-oxo centers required for oxo-bridge formation. The syntheses and properties of these complexes, the X-ray structure of one of the complexes, and the ability of various ligand structures to inhibit dimerization upon electrochemical reduction of the complexes are reported here.

Results

Complexes with bidentate NS, tridentate NOS, and tetradentate N_2O_2 and N_2S_2 ligands with five basic structures have been synthesized (Table I). In all cases where $\text{R} \neq \text{H}$, examination of stereo models indicates some degree of steric interaction between ligands in Mo(V) oxo-bridged dimers is to be expected.

Electrochemistry. All complexes exhibit an irreversible reduction peak in their cyclic voltammograms at a negative potential (−0.99 to −1.65 V vs. SCE; Table II). This peak

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