Table I. ^{51}V Chemical Shifts in Vanadium(V) Imido Species[a]

complex	chem shift, ppm	$\Delta\nu_{1/2}$, Hz
$V(Ntol)Cl_3$	305	500
$V(Ntol)Cl_3(THF)$	374	1900
$V(Ntol)Cl_3(PPh_3)$	392	700
$V(Ntol)Cl_2(O\text{-}t\text{-}Bu)$	−171	500
$V(Ntol)Cl(O\text{-}t\text{-}Bu)_2$	−472	390
$V(Ntol)(O\text{-}t\text{-}Bu)_3$	−654[b]	90
$V(Ntol)(\eta^5\text{-}C_5H_5)Cl_2$	−240	790

[a] Chemical shifts relative to external $VOCl_3/CDCl_3$ (75% v/v). Positive values denote downfield shifts. All spectra were determined as $CDCl_3$ solutions at 105.2 MHz at 25 °C. (b) This signal is a triplet with $^1J_{^{14}N-^{51}V} = 111$ Hz.

displayed by the isoelectronic $VOCl_3$ species that typically forms diadducts of the form $VOCl_3\cdot 2L$.[7]

Preliminary studies have revealed that the chloride ligands in **1** are prone to substitution under mild conditions. Thus, the room-temperature reaction of **1** with 1, 2, or 3 equiv of potassium *tert*-butoxide in THF affords the imido alkoxides $V(Ntol)Cl_2(O\text{-}t\text{-}Bu)$[8], $V(Ntol)Cl(O\text{-}t\text{-}Bu)_2$,[9] and $V(Ntol)(O\text{-}t\text{-}Bu)_3$[10] as purple, orange, and yellow crystals, respectively. The reaction of **1** with NaC_5H_5 in THF yields $(\eta^5\text{-}C_5H_5)V(Ntol)Cl_2$,[11] a rare[12] example of an organometallic derivative of vanadium(V).

We have also examined the ^{51}V NMR spectra of **1** and its derivatives (Table I). Until now, the only ^{51}V chemical shift data reported for vanadium(V) complexes has concerned oxo species.[13] Inspection of the data in Table I reveals that the substitution of the *p*-tolylimido group for an oxo ligand has a dramatic effect on both the ^{51}V chemical shift and the line widths of the resonances (cf. the data for **1** with δ 305 and $\Delta\nu_{1/2} = 500$ Hz vs. $VOCl_3$ with δ 0 and $\Delta\nu_{1/2} = 23$ Hz). The downfield chemical shifts observed for **1** and its Lewis base adducts are unusual in ^{51}V NMR spectroscopy; the only other species known to resonate in this region is $VOBr_3$. In ^{51}V NMR studies of VOX_3 species (X = F, Cl, Br), it has been established that V(V) is one of the few nuclei to display an inverse halogen dependence, i.e., $\delta(OVBr_3) < \delta(OVCl_3) < \delta(OVF_3)$. This ordering has been interpreted in terms of decreasing paramagnetic contributions to the nuclear shielding constant.[13d] The intense colors of **1** and its derivatives (which, in these d^0 complexes, must arise from charge transfer) connote the presence of low-lying electronic excited states, thus implying a large paramagnetic component in their nuclear shieldings. We attribute the relatively large line widths observed for the present complexes to enhanced quadrupolar broadening ($Q(^{51}V) = 0.3$ b) as a result of the lowering of symmetry (assumed to be C_s) imposed by the *p*-tolylimido group. Except in the case of $V(Ntol)(O\text{-}t\text{-}Bu)_3$, the line widths observed are sufficiently large so as to obscure $^{51}V-^{14}N$ coupling, which has been reported to be 95 Hz in the compound $V(N\text{-}t\text{-}Bu)(OSiMe_3)_3$.[1d,14]

Further studies of the spectroscopy and reactivity of these and related species are in progress.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Bureau of General Research at Kansas State University for support of this research. We thank Dr. W. A. Nugent and Dr. T. H. Tulip of E. I. du Pont de Nemours and Co., Inc., for helpful discussions. The WM-400 NMR spectrometer employed in this work was purchased with the assistance of an NSF instrumentation award.

Registry No. **1**, 90941-76-7; $V(Ntol)Cl_3(THF)$, 90941-80-3; $V(Ntol)Cl_3(PPh_3)$, 90941-81-4; $V(Ntol)Cl_2(O\text{-}t\text{-}Bu)$, 90941-77-8; $V(Ntol)Cl(O\text{-}t\text{-}Bu)_2$, 90941-78-9; $V(Ntol)(O\text{-}t\text{-}Bu)_3$, 90941-79-0; $V(Ntol)(\eta^5\text{-}C_5H_5)Cl_2$, 90941-82-5; $VOCl_3$, 7727-18-6; *p*-tolyl isocyanate, 622-58-2.

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(8) Anal. Calcd for $C_{11}H_{16}NOCl_2V$: C, 44.03; H, 5.37; N, 4.67. Found: C, 44.26; H, 5.33; N, 4.80. ^1H NMR ($CDCl_3$, 25 °C): δ 7.19 (q, 4 H, J_{AB} = 8.2 Hz, $C_6H_4CH_3$), 2.42 (s, 3 H, $C_6H_4CH_3$), 1.61 (s, 9 H, $OC(CH_3)_3$).

(9) Anal. Calcd for $C_{15}H_{25}NO_2ClV$: C, 53.34; H, 7.46; N, 4.15. Found: C, 53.29; H, 7.49; N, 4.59. ^1H NMR ($CDCl_3$, 25 °C): δ 7.11 (q, 4 H, J_{AB} = 8.3 Hz, $C_6H_4CH_3$), 2.36 (s, 3 H, $C_6H_4CH_3$), 1.50 (s, 18 H, $OC(CH_3)_3$).

(10) Anal. Calcd for $C_{19}H_{34}NO_3V$: C, 60.79; H, 9.13; N, 3.73. Found: C, 60.93; H, 9.05; N, 3.90. ^1H NMR ($CDCl_3$, 25 °C): δ 7.08 (q, 4 H, J_{AB} = 8.3 Hz, $C_6H_4CH_3$), 2.33 (s, 3 H, $C_6H_4CH_3$), 1.42 (s, 27 H, $OC(CH_3)_3$).

(11) This procedure yields $(\eta^5\text{-}C_5H_5)V(Ntol)Cl_2$ as black microcrystals. We have not yet succeeded in obtaining an analytical sample of this material, owing to the presence of a persistent impurity that appears at δ 1.26 (s) in the ^1H NMR spectrum. The intensity of this peak is ca. 5% of the C_5H_5 resonance. Alternative synthetic routes are being explored. ^1H NMR ($CDCl_3$, 25 °C): δ 7.13 (q, 4 H, J_{AB} = 8.0 Hz, $C_6H_4CH_3$), 6.58 (s, 5 H, C_5H_5), 2.44 (s, 3 H, $C_6H_4CH_3$).

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(14) Note, however, that the complex $V(N\text{-}t\text{-}Bu)(OSiMe_3)_3$ should possess C_{3v} symmetry and consequently a relatively narrow ^{51}V resonance, thus permitting the observation of coupling to ^{14}N.

Characterization of a True Intermediate-Spin (Porphinato)iron(III) Complex

Sir:

Intermediate-spin (porphinato)iron(III) complexes have been accorded considerable interest. Their properties may be relevant to the behavior of certain biologically important heme-containing proteins,[1-4] and the physical chemistry of this infrequently encountered species is not well described.

At ambient temperatures, all of the intermediate-spin (tetraarylporphinato)iron complexes reported to date are accurately characterized as quantum-mechanical $S = {}^3/_2, {}^5/_2$ spin-state admixtures.[5-8] If one starts from a high-spin ferric configuration, the $S = {}^3/_2, {}^5/_2$ admixture is attained through weak axial ligation of the perchlorate ion. Porphyrin core contraction that accompanies an increased attraction between iron and the pyrrole nitrogens destabilizes the iron $d_{x^2-y^2}$ atomic orbital to the extent that partial demotion of the electron to

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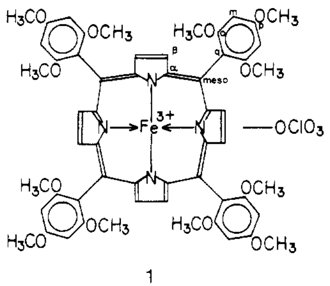

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Figure 1. Structural diagram of [TPP(2,4,6-OCH_3)]$FeClO_4$, showing designations for phenyl and porphyrin positions used in reporting NMR data.

d_{xy} is favored.[6,7,9] One consequence of this description of the spin-state admixture is that steric interactions that hinder the approach of axial ligands to iron should enhance the $S = {}^3/_2$ component in the admixture through further core contraction resulting from the weakened axial coordination. Additional destabilization of $d_{x^2-y^2}$ might also be expected by substitution on the porphyrin periphery with groups that increase electron density in the porphyrin 3e(π) molecular orbital which undergoes repulsive interactions with $d_{x^2-y^2}$. Weak axial ligation, hindered approach to iron, and strongly electron-releasing peripheral substituents are all features of (perchlorato)(tetrakis(2,4,6-trimethoxyphenyl)porphinato)iron(III) (**1**), leading to the expectation that the iron $d_{x^2-y^2}$ orbital could be sufficiently raised in energy to result in a true intermediate-spin complex. We report the preparation of **1** (Figure 1) and confirmation that its spectroscopic and magnetic properties are consistent with its description as an $S = {}^3/_2$ species. The bis(tetrahydrofuran) complex **2** has also been characterized and is predominantly intermediate spin.

Experimental Section. All solvents used were purchased as reagent grade or better and were stored over 3A molecular sieves. A Bruker WM 250 operating at 250 MHz was used for the ^1H NMR and at 62.8 MHz for the ^{13}C NMR. Magnetic moments were determined by the Faraday balance technique at room temperature. ESR spectra were recorded on a Varian E-109 spectrometer at room temperature and 77 K using DPPH as a field marker. Mössbauer spectra were taken with a standard constant-acceleration spectrometer using iron foil as the reference spectrum.

The chloro[10-12] and hydroxo[13] complexes of (tetrakis-(2,4,6-trimethoxyphenyl)porphinato)iron(III) ([TPP(2,4,6-OCH_3)]Fe^+) were synthesized according to published methods. Procedures relating to synthesis and handling of the perchlorato complex were carried out under nitrogen in a drybox. [TPP(2,4,6-OCH_3)]$FeClO_4$ was synthesized by metathesis[7] of the chloride with anhydrous silver perchlorate in refluxing tetrahydrofuran (THF). Precipitation by addition of heptane gave a bis(tetrahydrofuran) adduct (**2**), which was obtained as the mono(chloroform) solvate on recrystallization from chloroform. Anal. Calcd for $FeC_{56}H_{52}N_4O_{16}Cl{\cdot}C_8H_{16}O_2{\cdot}CHCl_3$: C, 56.07; H, 4.96; N, 4.03; Fe, 4.03. Found: C, 55.66; H, 5.35; N, 4.38; Fe, 3.98. UV-vis ($CHCl_3$; λ_{max} (nm) ($\epsilon \times 10^{-4}$)): 398 (11.87), 520 (177).

Heating under vacuum (0.02 torr) at 60 °C followed by recrystallization from chloroform gave the unligated perchlorato complex (**1**) as the mono(chloroform) solvate. Anal. Calcd for $FeC_{56}H_{52}N_4O_{16}Cl{\cdot}CHCl_3$: C, 54.87; H, 4.28; N, 4.49; Fe, 4.47. Found: C, 54.92; H, 5.15; N, 4.44; Fe, 4.37. UV-vis ($CHCl_3$; λ_{max} (nm) ($\epsilon \times 10^{-4}$)): 398 (18.50), 525 (2.10).

Table I. ^1H NMR Spectra of [TPP(2,4,6-OCH_3)]Fe^+ Complexes[a]

anion	py H	m-H		o-OCH_3		p-OCH_3	ligand	
Cl^-	78.5	13.8	12.5	5	3	5		
OH^-	79.3	11.1	10.3	4.5	3.3	4.7	0	
$ClO_4^-{\cdot}2THF$	−28.0	9.2		3.6		5.0	10.1	19.5
ClO_4^-	−30.6	9.1		3.5		4.7		

[a] Spectra run in chloroform-*d*, 250 MHz, ambient temperature. Shifts are reported in ppm relative to Me_4Si.

Table II. Comparison of ^{13}C NMR Shifts of (Perchlorato)(tetraarylporphinato)iron(III) Complexes[a]

Ph substituent	pyrrole β	pyrrole α	meso	Ph o	Ph m	Ph p	Ph q	substituent
2,4,6-OCH_3	91	60	238	218	95	166	30	58, 57
4-OCH_3[15]	580	363	363	299	123	171	12	57
4-H[15]	634	438	368	301	143	140	21	
4-Cl[15]	680	508	352	299	140	147	21	
4-CF_3[15]	790	661	346	301	139	141	25	122[b]

[a] All ^{13}C NMR spectra were run at 62.8 MHz in chloroform-*d* at ambient temperature. Shifts are reported in ppm relative to Me_4Si. [b] Quartet with J_{C-F} = 269 Hz.

Table III. ^{57}Fe Mössbauer Data (Microcrystalline State, 295 K)

complex	isomer shift, mm/s (δ)	quadrupole splitting, mm/s (dEq2)
[TPP(2,4,6-OCH_3)]$FeClO_4{\cdot}CHCl_3$	0.41	3.55
[TPP(2,4,6-OCH_3)]$FeClO_4{\cdot}2THF{\cdot}CHCl_3$	0.39	3.28

Results and Discussion. On coordination of the perchlorate ion, the ^1H NMR spectra of (tetrakis(2,4,6-trimethoxyphenyl)porphinato)iron(III) complexes (Table I) show the marked upfield shift of the pyrrole β-proton resonance that is diagnostic for vacancy of the iron $d_{x^2-y^2}$ atomic orbital. The appearance of the pyrrole signals of **1** and **2** upfield from Me_4Si in the same region as the pyrrole resonances of low-spin ferric complexes[14] suggests little if any occupancy of $d_{x^2-y^2}$ in **1** and **2**. This conclusion is reinforced by a comparison of the pyrrole proton shifts of **1** and **2** with those observed for truly spin-admixed (tetraarylporphinato)iron(III) complexes in halocarbon solvents, which range from 26 ppm ([TPP(4-CF_3)]$FeClO_4$) to 5 ppm ([TPP(4-OCH_3)]$FeClO_4$) downfield from Me_4Si.[7,15] The hexacoordinate complex formed with THF (**2**) contains a small high-spin component as indicated by the downfield shift of the pyrrole proton (Table I), although **2** is still predominantly intermediate spin. The role of the ortho methoxy groups in preventing strong axial binding may be reflected in the observations that **2** is the only perchlorato complex prepared in our laboratory from which THF could be removed by heating under vacuum and that the analogous (TPP)$FeClO_4{\cdot}2THF$ complex[16] is predominantly high spin.

Although correlation of ^{13}C NMR shifts with electronic structure is less well characterized,[17,18] the virtual vacancy of $d_{x^2-y^2}$ in **1** is evident in the upfield location of the pyrrole α-

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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 ^{1}H 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 ^{1}H 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 μ_{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-OCH$_3$)]FeClO$_4$ 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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Comment on Two Papers by R. H. Magnuson concerning Osmium(V) Compounds. Synthesis of SCl$_3$[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 PPh$_4$[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 AsPh$_4$[OsCl$_6$] by the reaction of OsCl$_5$ with AsPh$_4$Cl in a C$_2$F$_3$Cl$_3$ suspension.[3] Meanwhile, Preetz and Bruns described still another method of synthesis by chlorination of NEt$_4$[Os(CO)$_4$Cl$_2$] at 130 °C.[4] Infrared[3,4] and resonance Raman[4] as well as ultraviolet/visible[4] 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] Os$_2$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 PPh$_4$[Cl$_5$OsNC(CCl$_3$)NCCl(CCl$_3$)]·CH$_2$Cl$_2$,[6] in which the Os–Cl bonds are found to be slightly longer than in PPh$_4$[OsCl$_6$].[2]

The reported crystal structure of PPh$_4$[OsCl$_6$] shows it to be isostructural with PPh$_4$[NbCl$_6$],[7] which is very closely related to the well-known and frequently encountered AsPh$_4$[RuNCl$_4$] structure type, crystallizing in the space group *P*4/*n*.[8] Packing conditions in PPh$_4^+$ and AsPh$_4^+$ salts have been thoroughly studied.[8] In the specific case of PPh$_4$[NbCl$_6$],[7] exactly the same situation as in PPh$_4$[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 PPh$_4$[NbCl$_6$] and has been found similarly in other compounds such as AsPh$_4$[ReCl$_4$(NO)$_2$][9] and AsPh$_4$[WSCl$_5$].[10] In AsPh$_4$[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. SCl$_3^+$[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:

$$\mathrm{OsO_4 + 5SCl_2 + {}^7/_2Cl_2 \rightarrow SCl_3[OsCl_6] + 4SOCl_2}$$

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

$$\mathrm{SCl_3[OsCl_6] \xrightleftharpoons[20\,°C]{70\,°C} {}^1/_2Os_2Cl_{10} + SCl_2 + Cl_2}$$

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