TABLE IV

QUANTITIES USED IN CALCULATING BONDING COEFFICIENTS

Quantity	MoOBr$_5$[a]	CrOCl$_5$[a]
λ_M, cm^{-1}	820[b]	275[c]
λ_L, cm^{-1}	2460[d]	587[b]
$\Delta E(b_2 - b_1)$, cm^{-1}	21,800.0[d]	23,200.0[e]
$\Delta E(b_2 - e)$, cm^{-1}	14,290.0[d]	13,200.0[e]
S_{b_2}	0.12[b]	0.12
S_e	0.16	0.16
S_{b_1}	0.20	0.20
K	0.9[b]	0.6[e]
P, cm^{-1}	−0.0055[b]	−0.00397[f]

[a] Reference 2. [b] Reference 1. [c] T. M. Dunn, *Trans. Faraday Soc.*, **57,** 1441 (1961). [d] Reference 6. [e] Reference 11. [f] Reference 18.

are $\beta_2 = 0.932$, $\epsilon = 0.844$, and $\beta_1 = 0.596$ for $MoOBr_5^{2-}$ and 0.886, 0.958, and 0.952 for $CrOCl_5^{2-}$. Although no trend is noted in the coefficients for $\beta_2(d_{xy})$, regular decreases in ϵ and β_1 are recorded in passing from fluoride[1] to chloride[1] to bromide.

By use of Mulliken population analysis one can then calculate spin densities and we find 3.3% for equatorial halide in $MoOCl_5^{2-}$ and 5.3% for $CrOCl_5^{2-}$.

TABLE V

BONDING COEFFICIENTS

Coefficient	$MoOBr_5^{2-}$	$CrOCl_5^{2-}$
β_2	0.932	0.886
ϵ	0.844	0.958
β_1	0.596	0.592

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The Preparation and Optical and Electron Spin Resonance Spectra of Some Hexachloro- and Pentachloroalkoxovanadates(IV)

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Several compounds of the type $[R_4N]_2V(OR')Cl_5$ have been prepared from $[(CH_3)_4N]_2VCl_6$ and $[(CH_3CH_2)_4N]_2VCl_6$. All compounds show normal, spin-only paramagnetism for a d^1 ion at room temperature. The magnetic moments for the alkoxo complexes vary little with temperature. Electronic, infrared, and electron spin resonance spectra have been measured. Bonding coefficients for the pertinent molecular orbitals have been calculated. $N_{\pi_2}{}^2$ and $N_{\sigma_2}{}^2$ decrease with increasing length of alkoxo chain while $N_{\pi_1}{}^2$ increases. Spin densities have been calculated for the equatorial Cl atoms from the bonding parameters.

Much recent interest has centered on the investigation of d^1 transition elements involving oxy ions of the type MO^{n+} where $M^{(n+2)+}$ is Cr^{5+}, Mo^{5+}, or V^{4+}. The halide complexes of these ions have been studied carefully and it is well established that there is substantial π bonding between the metal and oxygen atom.[1-5] Recent work in this laboratory has concerned the preparation and characterization of d^1 transition element alkoxides and complexes containing alkoxides as ligands.[6-12] It was decided that vanadium(IV) chloride alkoxides would be of interest because of the large amount of work which has been done with the vanadyl systems. The monoalkoxide species ought to be six-coordinate anions where the metal to oxygen bond is formally a single bond. A study of these compounds should show the effect on the bonding parameters of changing the donating strength of the oxygen by varying the alkoxide group. The effect of changing the halogen from F$^-$ to Cl$^-$ to Br$^-$ has been shown in the case of $MoOX_5^{2-}$.[1,2]

Bradley and Mehta[13] and Thomas[14] have prepared a number of vanadium alkoxides of the type $V(OR)_4$. Various investigators have isolated substances of the general form $V(OR)_2Cl_2 \cdot ROH$ from alcoholic solutions.[15-17] Several salts of the hexachlorovanadate ion

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have been prepared by Kilty and Nicholls[18] and by Fowles and Walton.[19] Gordon, *et al.*, have investigated the esr spectra of $V(OC_4H_9)_4$.[20] Our purpose has been to prepare and characterize theoretically interesting vanadium(IV) complexes.

Experimental Section

Materials.—Vanadium tetrachloride was prepared by elementary synthesis. Vanadium metal powder (m2N8) was obtained from Alfa Inorganics, Inc. The reaction took place in a tube furnace at 390° and the liquid VCl_4 was condensed in an ice bath. The VCl_4 was distilled under a chlorine atmosphere and degassed. *Anal.* Calcd for VCl_4: V, 26.43. Found: V, 26.14.

Methyl and ethyl alcohol were dried by reaction with magnesium and subsequent distillation. Both *n*-propyl and *n*-butyl alcohols were reagent grade and used without further purification. Reagent grade ethyl ether was stored over sodium wire. Acetonitrile was distilled three times from phosphorus pentoxide and stored under nitrogen. Carbon tetrachloride and methylene chloride were continuously refluxed over calcium hydride and distilled as needed. Thionyl chloride was reagent grade and used without further purification.

Tetramethylammonium chloride was obtained from Eastman Organic Chemicals and dried at 110° before use. Tetraethylammonium chloride was also obtained from Eastman Organic Chemicals and used without further treatment.

Pure nitrogen was obtained by passing Matheson prepurified nitrogen through a 3-ft BTS[21] column and subsequently through calcium chloride and barium oxide drying towers.

$[(CH_3)_4N]_2VCl_6$.—$(CH_3)_4NCl$ (5.0 g) was dissolved in approximately 50 ml of thionyl chloride. A solution consisting of 3 ml of VCl_4 in 20 ml of thionyl chloride was added and the solution was stirred during the addition. A red-black precipitate formed immediately. The precipitate was extremely fine and the solution was difficult to filter. The product was washed with CCl_4 and dry ether and dried under vacuum. *Anal.* Calcd for $VCl_6C_8H_{24}N_2$: V, 12.37; Cl, 51.65; C, 23.31; H, 5.87; N, 6.80. Found: V, 12.34; Cl, 51.65; C, 23.01; H, 5.68; N, 6.68.

$[(CH_3)_4N]_2V(OCH_3)Cl_5$.—$[(CH_3)_4N]_2VCl_6$ (2.7 g) was dispersed in a solution of 20% acetonitrile in ether. (The reaction also takes place in methylene chloride or nitromethane.) One equivalent of methanol was added while the solution was being stirred. The reaction proceeded immediately with formation of a golden product. HCl gas could be detected above the reaction vessel. The product was stirred 1 hr, filtered under nitrogen, washed with warm acetonitrile and ether, and dried under vacuum. *Anal.* Calcd for $VCl_5C_9H_{27}N_2O$: V, 12.50; Cl, 43.50; C, 26.50; H, 6.68. Found: V, 12.60; Cl, 43.56; C, 26.44; H, 6.78.

$[(CH_3)_4N]_2V(OC_2H_5)Cl_5$.—This and subsequent alkoxides were prepared in the same manner as the above methoxo complex. *Anal.* Calcd for $VCl_5C_{10}H_{29}N_2O$: V, 12.09; Cl, 42.06; C, 28.47; H, 6.94. Found: V, 12.20; Cl, 42.03; C, 28.56; H, 6.98.

$[(CH_3)_4N]_2V(OC_3H_7)Cl_5$.—*Anal.* Calcd for $VCl_5C_{11}H_{31}N_2O$: V, 11.70; Cl, 40.71. Found: V, 11.69; Cl, 40.67.

$[(CH_3)_4N]_2V(OC_4H_9)Cl_5$.—*Anal.* Calcd for $VCl_5C_{12}H_{33}N_2O$: V, 11.33; Cl, 39.44. Found: V, 11.22; Cl, 39.21.

$[(C_2H_5)_4N]_2VCl_6$.—$(C_2H_5)_4NCl$ (9.0 g) was dissolved in approximately 40 ml of thionyl chloride and was stirred and a solution consisting of 3 ml of VCl_4 in 20 ml of thionyl chloride was added. A red-black oil was obtained immediately. Stirring was continued and approximately 100 ml of CCl_4 was added slowly. A red-black crystalline precipitate was obtained. The precipitate was filtered under nitrogen, washed with dry CCl_4 and ether, and dried under vacuum. *Anal.* Calcd for $VCl_6C_{16}H_{40}N_2$: V, 9.72; Cl, 40.60; C, 36.64; H, 7.69. Found: V, 9.51; Cl, 40.47; C, 36.31; H, 7.83.

$[(C_2H_5)_4N]_2V(OCH_3)Cl_5$.—*Anal.* Calcd for $VCl_5C_{17}H_{43}N_2O$: V, 9.81; Cl, 34.12. Found: V, 9.81; Cl, 34.10.

$[(C_2H_5)_4N]_2V(OC_2H_5)Cl_5$.—*Anal.* Calcd for $VCl_5C_{18}H_{45}N_2O$: V, 9.55; Cl, 33.22. Found: V, 9.70; Cl, 33.41.

$[(C_2H_5)_4N]_2V(OC_3H_7)Cl_5$.—*Anal.* Calcd for $VCl_5C_{19}H_{47}N_2O$: V, 9.30; Cl, 32.36. Found: V, 9.20; Cl, 32.17.

Some Reactions of the Hexachloro- and Pentachloroalkoxovanadates.—All of the above compounds are sensitive to moisture and oxygen. The hexachlorovanadates are also sensitive to light. All dissolve in water to form a blue color, which may be attributed to the VO^{2+} ion.

The alkoxides react with thionyl chloride to give the hexachlorovanadates. Presumably a reaction occurs similar to that used by Fowles[19] in the preparation of hexachlorovanadates from vanadyl salts

$$2V(OR)Cl_5^{2-} + SOCl_2 \longrightarrow 2VCl_6^{2-} + RO\overset{\overset{\displaystyle O}{\|}}{S}OR$$

If solutions of the monoalkoxide in acetonitrile are saturated with HCl, the hexachlorovanadate species are formed. An equilibrium

$$VCl_6^{2-} + ROH \rightleftarrows V(OR)Cl_5^{2-} + HCl$$

must exist in solution.

Attempts to make the tetraethylammonium pentachloro(*n*-butoxo)vanadate(IV) as well as various other alkoxides have not been successful. Cyclohexanol, 2-propanol, *t*-butyl alcohol, and 1-octanol do not react with the hexachlorovanadate ion to any appreciable extent. One assumes that steric factors may play an important role.

A green solution is obtained if the hexachlorovanadate salts are dissolved in methanol. When the solution is evaporated to dryness, only $VOCl_4^{2-}$ salts can be obtained. A reaction must take place similar to that reported earlier.[11,12]

$$VCl_6^{2-} + \text{excess } CH_3OH \longrightarrow V(OCH_3)_2Cl_4^{2-} + 2HCl$$

$$V(OCH_3)_2Cl_4^{2-} \longrightarrow VOCl_4^{2-} + CH_3OCH_3$$

Analyses.—Vanadium was determined by titration with standard permanganate in acidic solutions where the vanadium had been first oxidized by excess permanganate and then reduced to vanadium(IV) by SO_2. Direct titrations on solutions of the compounds confirmed the oxidation state IV.

Chloride was determined by the potentiometric titration with standard silver nitrate. Gravimetric chloride analyses were also carried out on several compounds. C, H, and N were determined by Spang Microanalytical Laboratories, Ann Arbor, Mich., which reported the compounds "hydrolyze very easily."

Experimental Methods.—All reactions were carried out in inert (dry N_2) atmospheres or under vacuum. Filtrations and washings were all performed by the application of nitrogen under pressure or by suction. All drying was *in vacuo* and compounds were stored under nitrogen in the absence of light.

Magnetic Moments.—Magnetic susceptibilities were measured by the Gouy method. The procedure was to determine the magnetic moment at room temperature and 77°K. In those cases where large changes occurred, the magnetic moment was also determined at 195°K. All samples were measured at several field strengths to check for ferromagnetism. Pascal's[22] constants were used to correct the measurements for diamagnetism of the cations and ligands.

Spectroscopic Measurements.—The infrared spectra of the complexes were obtained by use of Nujol mulls and a Unicam Model SP-200 spectrophotometer (5000–650 cm^{-1}) and a Beckman IR-7 spectrophotometer (700–200 cm^{-1}). The visible

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TABLE I

OPTICAL SPECTROSCOPIC FEATURES OF THE HEXACHLORO AND PENTACHLOROALKOXO COMPOUNDS OF VANADIUM(IV)

Compound	Electronic absorption max × 10^{-3}, cm^{-1} (ϵ in parentheses)		Electronic absorption reflectance max × 10^{-3}, cm^{-1}	Ir absorption max, cm^{-1}
	(CH_3CN)	CH_2Cl_2		
$[(CH_3)_4N]_2VCl_6$	13.8 sh		15.2	1490, 1290, 996, 960, 465, 295
	15.3 (70)			
	21.2 (330)		19.4	
	37.5		22.5	
$[(CH_3)_4]_2V(OCH_3)Cl_5$	13.5 (3.0)		13.3	1490, 1290, 1090, 996, 960, 605, 458, 240
	14.5 (3.4)		14.5 vw	
	26.1 (1250)		24.8 vw	
	~41.0		28.6	
$[(CH_3)_4]_2V(OC_2H_5)Cl_5$	13.5 (2.3)		13.4	1490, 1290, 1085, 1050, 990, 935, 600, 468, 240
	14.8 (2.6)		15.5 vw	
	26.1 (1230)		26.0	
	~41.0			
$[(CH_3)_4]_2V(OC_3H_7)Cl_5$	13.4 (2.1)		13.6	1490, 1300, 1060, 970, 706, 575, 462, 390, 380, 240
	14.8 (2.3)		15.4 vw	
	26.1 (1070)		26.0	
	~40.0			
$[(CH_3)_4]_2V(OC_4H_9)Cl_5$	13.5 (2.0)		13.7	1490, 1300, 1090, 1010, 970, 700, 460
	14.4 (2.0)		15.5 vw	
	26.1 (1030)		26.0	
	~40.0			
$[(C_2H_4)_4N]_2VCl_6$	15.4 (116)		15.2	1195, 1019, 805, 412, 385, 380, 370
	21.2 (1150)		15.5	
	37.3 (2670)		17.8	
	~41.0		20.6	
			22.8	
$[(C_2H_5)_4N]_2V(OCH_3)Cl_5$	13.7	14.3 (8.0)	13.8	1195, 1080, 1010, 805, 420, 390
	14.9	26.0 (2000)	15.5 vw	
	~37.9	~40.0	27.0	
$[(C_2H_5)_4N]_2V(OCH_2H_5)Cl_5$	13.3	14.4 (9.7)	14.1	1195, 1090, 1040, 1010, 805, 425, 390, 230
	15.0	26.2 (1420)	15.5 vw	
	25.9	~40.0	28.5	
	~37.8			
$[(C_2H_5)_4N]_2V(OC_3H_7)Cl_5$	13.5	14.5 (9.5)	14.3	1195, 1050, 1010, 805, 490, 425, 390, 370, 240
	14.9	26.3 (1490)	15.5 vw	
	25.9	~40.0	28.5	
	~37.8			

TABLE II

MAGNETIC MOMENTS AND SOME RELATED PROPERTIES

	μ, BM							
	295°K	195°K	77°K	θ, °K	ξ	κ	ν	Δ
$[(CH_3)_4]_2VCl_6$ (I)	1.73	1.53	1.32		160–170	0.8–0.85	2	320–340
$[(CH_3)_4N]_2V(OCH_3)Cl_5$ (II)	1.79		1.76	−6				
$[(CH_3)_4N]_2V(OC_2H_5)Cl_5$ (III)	1.79		1.76	−6				
$[(CH_3)_4N]_2V(OC_3H_7)Cl_5$ (IV)	1.77		1.72	−4				
$[(CH_3)_4N]_2V(OC_4H_9)Cl_5$ (V)	1.79		1.74	−7				
$[(C_2H_5)_4N]_2VCl_6$ (VI)	1.74	1.57	1.32		160–170	0.8–0.85	2	320–340
$[(C_2H_5)_4N]_2V(OCH_3)Cl_5$ (VII)	1.78		1.75	−3				
$[(C_2H_5)_4N]_2V(OC_2H_5)Cl_5$ (VIII)	1.77		1.72	−4				
$[(C_2H_5)_4N]_2V(OC_3H_7)Cl_5$ (IX)	1.75		1.72	−2				

and ultraviolet spectra were obtained by means of a Unicam Model SP-800 spectrophotometer and a Cary Model 14 spectrophotometer. The visible–ultraviolet spectra were determined in either methylene chloride or acetonitrile by preparing the compound in solution. Reflectance spectra were determined by means of a Baush and Lomb Spectronic 600 spectrophotometer with diffuse reflectance attachment. X-Band electron spin resonance spectra at room temperature and 100°K were determined as before.[9]

Results and Discussion

Table I gives the important spectroscopic features of the compounds which were prepared. The peak at $\sim 15.5 \times 10^3\ cm^{-1}$ for the hexachlorovanadates is the ${}^2T_{2g} \rightarrow {}^2E_g$ transition. The other two peaks are charge-transfer bands. The two peaks at ~13.5 and ~14.5 cm^{-1} for the alkoxides are probably the ${}^2B_2 \rightarrow {}^2E$ and ${}^2B_2 \rightarrow {}^2B_1$ transitions, respectively. The ${}^2B_2 \rightarrow {}^2A_1$ transition is probably masked by the two charge-transfer bands. In Table II are given the magnetic moments and some related quantities for each compound. The magnetic moments of the alkoxides show little temperature dependence and their Weiss constants are therefore small. The magnetic moments of the hexachlorovanadates show a strong temperature dependence. The shoulder on the $^2T_{2g} \rightarrow {}^2E_g$ transition observed in the uv spectrum for the hexachlorovanadates represents a removal of the degeneracy of the ground state by axial distortion to give tetragonal symmetry. Thus, it is possible to employ the calculations outlined by Figgis[23] to obtain K (a measure of the delocalization of the 3d^1 electron on the ligand), Δ (the separation between the orbital levels of $^2T_{2g}$ created by tetragonal distortion of the ligand field), and ν (which is Δ/ξ where ξ is the spin–orbit coupling constant). These values agree with similar calculations by Machin and Murray.[24] The value of 160–170 cm^{-1} for ξ indicates the formal charge on the hexachlorovanadates has been reduced to approximately 2+.[25]

No esr signal was observed for the hexachlorovanadates in the solid or in $SOCL_2$ at 297 or 77°K. In fact, the metal hyperfine structure of the alkoxides could be observed in diluted powders of $V(OR)Cl_5^{2-}$ in VCl_6.$^{2-}$ However, these spectra were not investigated further. Electron spin resonance spectra were obtained for the alkoxides as pure powders at 297°K and as solutions at 297 and 100°K (glasses). The V metal hyperfine splitting was observed. The solution spectra consisted of eight lines ($I = {}^7/_2$). Spectra of the glasses could be resolved into parallel and perpendicular components.

Since the hyperfine splittings are on the order of 100 G, the high-field approximation cannot be applied rigorously. The perturbation of the Zeeman transition resulting from the hyperfine interaction was corrected by means of the following equations

$$h\nu = g\beta H_0 \qquad (1)$$

for isotropic g

$$H_0 = H_m + \langle a\rangle m_I + \frac{\langle a\rangle^2}{2H_m}[I(I+1) - m_I^2] \qquad (2)$$

for $g_{||}$

$$H_0 = H_m + A_{||}m_I + \frac{A_\perp^2}{2H_m}[I(I+1) - m_I^2] \qquad (3)$$

for $g_\perp$

$$H_0 = H_m + A_\perp m_I + \left(\frac{A_{||}^2 + A_\perp^2}{4H_m}\right)[I(I+1) - m_I^2] \qquad (4)$$

where H_m is the magnetic field position of the esr line due to the component m_I of the nuclear spin I, ν is the klystron frequency, and $\langle a\rangle$, $A_{||}$, and $A_\perp$ are the hyperfine splitting constants. The corrections are necessarily reiterative and were carried out by desk calculator. Normally three iterations were sufficient. The hyperfine splitting constants were determined from the positions of the fourth and fifth, third and sixth, second and seventh, and first and eighth lines where resolution permitted. The values of $\langle a\rangle$, $A_{||}$, $A_\perp$, $\langle g\rangle$, $g_\perp$, and $g_{||}$ are given in Table III.

TABLE III

ESR PARAMETERS FROM SOLID AND FROZEN GLASS SPECTRA[a]

	$\langle g\rangle_{solid}$	$\langle g\rangle_{soln}$	$\langle a\rangle_{soln}$	$g_{\|\|}$	$g_\perp$	$A_{\|\|}$	$A_\perp$
II	1.949	1.9688	97.4	1.9478	1.9794	168.9	66.6
III	1.950	1.9696	97.1	1.9510	1.9788	167.5	65.0
IV	1.946	1.9698	97.0	1.9516	1.9786	166.3	64.6
V	1.946	1.9687	96.9	1.9519	1.9786	166.2	64.5
VII	1.946	1.9697	97.6	1.9493	1.9777	172.0	65.7
VIII	1.945	1.9696	96.8	1.9498	1.9767	169.2	64.7
IX	1.945	1.9696	96.7	1.9498	1.9777	167.8	63.8

[a] Hyperfine splittings are given 10^{-4} cm^{-1}.

The observed g and A values were used to calculate the coefficients in a simple molecular orbital scheme. The procedure was similar to that of Kuska and Rogers[5] except the contribution from charge-transfer bands was not included. The $V(OR)Cl_5^{2-}$ ion has one unpaired electron and the ground state of the ion is $^2B_2$. The orbitals which are necessary for discussion are those which are bases of the b_1, b_2, and e representations. The LCAO–MO wave functions of these orbitals are

$$|B_2\rangle^* = N_{\pi_2}(d_{xy} - \lambda_{\pi_2}\phi_{b2}) \qquad (5)$$

$$|B_1\rangle^* = N_{\sigma_2}(d_{x^2-y^2} - \lambda_{\sigma_2}\phi_{b1}) \qquad (6)$$

$$|E\rangle^* = N_{\pi_1}(d_{xz} \text{ or } d_{yz} - \lambda^e{}_{\pi_1}\phi^e{}_e - \lambda^a{}_{\pi_1}\phi^a{}_e) \qquad (7)$$

where the metal orbitals are d functions and $\lambda^e{}_{\pi_1}$ and $\lambda^a{}_{\pi_1}$ are the $xz(yz)$ molecular orbital coefficients for the equatorial and axial ligands, respectively. The ligand orbitals of oxygen and chlorine involved in π bonding are taken as pure p orbitals. The ligand orbitals involved in σ bonding were taken as sp hybrids.

The experimental g and A values can be related to the molecular orbitals by

$$g_{||} - 2.0023 = \frac{-8\xi N_{\pi_2}{}^2 N_{\sigma_2}{}^2}{\Delta(b_2 - b_1)}[1 - (1/2)(\lambda_{\pi_2}\lambda_{\sigma_2})T(n) - 2\lambda_{\sigma 2}S_{b1} - 2\lambda_{\pi_1}S_{b2}] \qquad (8)$$

$$g_\perp - 2.0023 = \frac{-2\xi N_{\pi_2}{}^2 N_{\pi_1}{}^2}{\Delta(b_2 - e)}[1 - (1\sqrt{2})(\lambda^e{}_{\pi_1}\lambda_{\pi_2}) - 2\lambda_{\pi_2}S_{b2} - \sqrt{2}\lambda^e{}_{\pi_1}S_{b2} - \lambda^a{}_{\pi_1}S_e] \qquad (9)$$

$$A_{||} - \langle a\rangle = \frac{4N^2{}_{\pi_2}P}{7} - \frac{8\xi N_{\pi_2}{}^2 N_{\sigma_2}{}^2 P}{\Delta(b_2 - b_1)} - \frac{6\xi N_{\pi_2}{}^2 N_{\pi_1}{}^1 P}{7\Delta(b_2 - e)} \qquad (10)$$

where S_{b1}, S_{b2}, and S_e are the metal–ligand overlap integrals. $T(n)$ is defined by Kivelson and Lee as

$$T(n) = n - \left(\frac{1}{3}\right)^{1/2}(1 - n^2)^1/_2 R\int_0^\infty r^2 R_{31}(r)\frac{d}{dr}[R_{30}(r)]dr$$

where R is the vanadium–ligand distance and $R_{31}(r)$ and $R_{30}(r)$ are the normalized radial 3p and 3s functions, respectively.[26] ξ is the spin–orbit coupling constant and $P = 2.0023 g_N \beta_e \beta_n \langle r^{-3}\rangle_{av}$, where β_e and β_n are the

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Bohr and nuclear magnetons, respectively, and g_N is the nuclear g factor. N_{π_2} and λ_{π_2} are related by the normalization requirement $N_{\pi_2}{}^2 = [1 - 4\pi_{\pi_2}S_{b2} + \lambda\pi_2{}^2]^{-1}$.

In order to solve for $N_{\pi_2}{}^2$, $N_{\sigma_2}{}^2$, and $N_{\pi_1}{}^2$ in the above equations, values must be obtained for ξ, P, $T(n)$, S_{b2}, S_{b1}, and S_e. The values of ξ and P depend on the formal charge which is assigned to the vanadium atom. In calculations involving the VO^{2+} group, most authors[5] feel the formal charge on the vanadium is reduced to approximately 2+. It would seem reasonable to assume the charge on the vanadium in the $V(OR)^{3+}$ group is approximately 3+. Thus[4] P is 1.50×10^{-2} cm^{-1}. ξ is taken from Dunn's tables as 210 cm^{-1}. $T(n)$ depends on the ligand σ-orbital hybridization. In our case where we have used sp hybrids for the σ bonding, $T(n)$ is estimated as 0.25.[26] The overlap terms were not determined but those values calculated for $VOCl_5{}^{2-}$ by Gutowsky should be very near the values for the alkoxides. Thus, S_{b2}, S_{b1}, and S_e were taken as 0.099, 0.165, and 0.139, respectively. The assumption was made that little charge occurs in the overlap terms in going from the methoxide to the butoxide. We also assumed $\lambda^a{}_{\pi_1} \approx \lambda^e{}_{\pi_1}$.

The values obtained by an iterative treatment of eq 8–10 are given in Table IV. A decrease in $N_{\pi_2}{}^2$ and $N_{\sigma_2}{}^2$ is observed in going from the methoxide to the butoxide ion and an increase is observed in $N_{\pi_1}{}^2$. The decrease in $N_{\pi_2}{}^2$ and $N_{\sigma_2}{}^2$ indicates that the B_2 and B_1 molecular orbitals become more covalent through the series. The increase in $N_{\pi_1}{}^2$ indicates the E molecular orbital becomes more ionic from $^-OCH_3$ to $^-OC_4H_9$.

TABLE IV

MOLECULAR ORBITAL COEFFICIENTS AND SPIN DENSITIES

	$N_{\pi 2}{}^2$	$N_{\pi 1}{}^2$	$N_{\sigma 2}{}^2$	$\lambda_{\pi 2}$	$\% f_\pi$
II	0.947	0.882	0.794	0.506	4.87
III	0.934	0.910	0.767	0.529	5.31
IV	0.921	0.924	0.751	0.552	5.75
V	0.919	0.924	0.739	0.555	5.81
VII	0.982	0.914	0.811	0.438	3.64
VIII	0.961	0.949	0.767	0.481	4.41
IX	0.944	0.955	0.765	0.512	4.99

The unpaired electron density in the four equatorial $3p_\pi$ orbitals of Cl^- is given by the Mulliken population analysis[27]

$$\begin{pmatrix}\text{unpaired electron density in} \\ \text{each ligand } 3p_\pi \text{ orbital}\end{pmatrix} = \frac{\lambda_{\pi_2}{}^2 N_{\pi_2}{}^2 - N_{\pi_2}{}^2 \lambda_{\pi_2} S_{b2}}{4}$$

The values obtained from this treatment are also given in Table IV. Manoharan and Rogers[1] and we, in our previous work,[2] have found excellent agreement between spin densities calculated in this manner and those calculated from ligand hyperfine splittings.

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Kinetics of Reduction of Neptunium(VI) with Disodium Ethylenediaminetetraacetate in Aqueous Perchloric Acid

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The kinetics for the reduction of neptunium(VI) with disodium ethylenediaminetetraacetate has been studied in aqueous perchlorate media. Stoichiometry, specific velocity constants, enthalpy of activation, and entropy of activation have been determined. A possible mechanism has been suggested which explains the observed kinetics and the stoichiometry of the reaction.

Introduction

Ethylenediaminetetraacetic acid (EDTA) has been reported to react with MnO_4^-, H_2O_2, Ce^{4+}, V^{5+}, and Cr^{6+}.[1-3] Disodium ethylenediaminetetraacetate ($Na_2H_2Y \cdot 2H_2O$) has been found to reduce plutonium(VI) as $PuO_2(ClO_4)_2$ to plutonium(V).[4] Further reduction is reported to take place slowly in a large excess of disodium EDTA. The following paper presents a kinetic study of the reaction of neptunium(VI) with disodium EDTA. This reaction was deemed important to the authors because of the similarity in behavior of Np(VI) and Pu(VI) as oxidizing agents.

Experimental Section

Stock solution of neptunium(VI) was prepared by electrolytic oxidation of a pure neptunium(V) solution in standard aqueous perchloric acid.[5] The course of oxidation was followed spectrophotometrically. Complete oxidation was ascertained by

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