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Pseudohalide and Chelate Complexes of Bis(cyclopentadienyl)vanadium(IV)[1,2]

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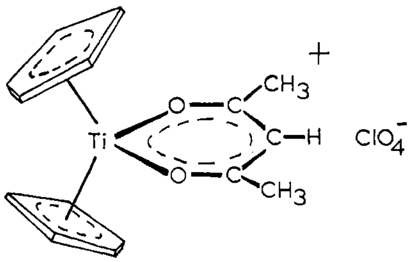
The compounds $(\pi\text{-}C_5H_5)_2VX_2$ have been synthesized with $X^- = N_3^-, NCO^-, CN^-, NCS^-$, and $NCSe^-$. In aqueous solution, $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$ reacts with bidentate ligands to give a series of compounds of the type $[(\pi\text{-}C_5H_5)_2VL]X^-$, where L is the conjugate base of acetylacetone, benzoylacetone, dibenzoylmethane, hexafluoroacetylacetone, or tropolone and where X^- is a large uninegative anion such as ClO_4^-, $F_3CSO_3^-$, $Cl_3CSO_3^-$, BF_4^-, $(C_6H_5)_4B^-$, PF_6^-, I^-, NCS^-, or $NCSe^-$. The effective magnetic moment of $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$ corresponds to the spin-only value for one electron, and the infrared spectrum indicates that the acetylacetonate ligand is chelating. The $\langle g \rangle$ values obtained from esr spectra are essentially the free-electron value for all of the compounds, and the hyperfine splitting constants are only slightly altered by variation in the ligands bound to the $(\pi\text{-}C_5H_5)_2V^{IV}$ moiety. The two compounds $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$ and $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$ appear to form isomorphous crystals.

Introduction

In an earlier communication,[4] we reported a study of the reactions of bis(cyclopentadienyl)titanium dichloride and diperchlorate with oxygen-containing bidentate ligands. Complexes of the type $[(\pi\text{-}C_5H_5)_2TiL]X$, where L was a bidentate ligand and X^- was ClO_4^- or $F_3CSO_3^-$ were easily synthesized. Conductivity measurements and infrared spectra indicated that the compounds were ionic and that the titanium atom was approximately tetrahedrally coordinated by the two cyclopentadienyl groups and the two oxygen atoms of the chelating ligand. Structure I was suggested for the acetylacetonate complex.



In this communication, we report an extension of these studies to the compounds of vanadium(IV). It was hoped that the behavior of the single unpaired electron of the bis(cyclopentadienyl)vanadium(IV) moiety would provide additional information on the nature of the bonding in these compounds. The first organometallic compounds of vanadium to be isolated and identified were the paramagnetic bis(cyclopentadienyl)vanadium dichloride and dibromide.[5,6] Upon oxidation of $(\pi\text{-}C_5H_5)_2VCl_2$ with a stream of Cl_2 and O_2 in $CHCl_3$ solution, $\pi\text{-}C_5H_5VOCl_2$ is obtained.[7] There appear to have been no other studies on the reactions of bis(cyclopentadienyl)vanadium(IV) with pseudohalides or with other oxygen- or nitrogen-containing ligands.

Experimental Section

Bis(cyclopentadienyl)vandium Dichloride, $(\pi\text{-}C_5H_5)_2VCl_2$.—This compound was prepared from vanadium tetrachloride and sodium cyclopentadienide in benzene by the method described by Skachilova, *et al.*[7]

Bis(cyclopentadienyl)vanadium Dicyanide, $(\pi\text{-}C_5H_5)_2V(CN)_2$.—To 100 ml of acetone were added $(\pi\text{-}C_5H_5)_2VCl_2$ (1 g, 0.004 mol) and NaCN (3 g, 0.06 mol). This mixture was boiled for 10 min, and the solvent was evaporated in a stream of air. The solid residue was extracted with 100 ml of boiling chloroform, and upon cooling of the chloroform solution green crystals of $(\pi\text{-}C_5H_5)_2V(CN)_2$ (0.75 g, 80%) formed and were collected on a frit. *Anal.* Calcd for $C_{12}H_{10}N_2V$: C, 61.8; H, 4.32. Found: C, 61.7; H, 4.10.[8] Infrared bands (cm^{-1}) were observed at 3106 s*, 2118 s, 2111 s, 1439 s*, 1429 s*, 1122 m*, 1020 s*, 1011 s*, 881 s, 858 vs, 845 vs*, 835 vs*, 478 m, 398 m, 368 m, 331 s, and 306 s. (An asterisk signifies $(\pi\text{-}C_5H_5)_2V^{IV}$ vibrations throughout this article.)

Bis(cyclopentadienyl)vanadium Diazide, $(\pi\text{-}C_5H_5)_2V(N_3)_2$.—To 100 ml of acetone were added $(\pi\text{-}C_5H_5)_2VCl_2$ (1 g, 0.004 mol) and NaN_3 (3 g, 0.05 mol). The solution was refluxed for 100 min, and the acetone was evaporated on a steam bath leaving a brown solid residue. This material was treated on a frit with 100 ml of water to remove excess NaN_3 and NaCl, and the brown $(\pi\text{-}C_5H_5)_2V(N_3)_2$ remaining (1.0 g, 93%) was washed with portions of water and then ether. The compound is very explosive. *Anal.* Calcd for $C_{10}H_{10}N_6V$: C, 45.3; H, 3.80. Found: C, 46.2; H, 3.98. Infrared bands (cm^{-1}) were observed at 3124 m*, 3112 m*, 3106 m*, 3082 m*, 2069 vs, 2028 vs, 1990 m, 1442 m*, 1432 m*, 1368 m, 1329 s, 1278 m, 1120 w, 1080 w, 1020 m*, 833 vvs*, 612 w, 590 m, 437 m, 392 w, 342 m, 303 w, and 262 vs.

Bis(cyclopentadienyl)vanadium Dicyanate, $(\pi\text{-}C_5H_5)_2V(OCN)_2$.—A slight excess of KOCN was added to a solution of $(\pi\text{-}C_5H_5)_2VCl_2$ (1 g, 0.004 mol) in 75 ml of water. The light green precipitate of $(\pi\text{-}C_5H_5)_2V(OCN)_2$ which formed immediately was collected on a frit and washed with large portions of water, ethanol, and ether successively; the yield was quantitative. *Anal.* Calcd for $C_{12}H_{10}N_2O_2V$: C, 54.4; H, 3.80. Found: C, 54.0; H, 3.57. Infrared bands (cm^{-1}) were observed at 3534 w, 3118 m*, 2248 vs, 2220 vs, 2165 m, 1440 s, b*, 1329 w, 1082 w, 1037 w*, 1017 m*, 832 vs*, 603 s, 591 s, 420 m, 389 m, 295 m, and 259 w.

Bis(cyclopentadienyl)vanadium Dithiocyanate, $(\pi\text{-}C_5H_5)_2V(NCS)_2$.—To a solution of $(\pi\text{-}C_5H_5)_2VCl_2$ (1 g, 0.004 mol) in

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[2] Taken from a thesis submitted by G. D. to the Graduate School of the University of Minnesota for the Ph.D. degree.

[3] NASA Trainee, 1965–1967.

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[7] S. Ya Skachilova, A. Savitskii, and R. Ya. Vlaskina, *Zh. Obshch. Khim.*, **36**, 1059 (1966).

[8] Microanalyses by Clark Microanalytical Laboratory, Urbana, Ill.

100 ml of water was added a fivefold excess of KNCS. The green precipitate which formed immediately was collected on a frit and washed successively with large portions of water, ethanol, and ether; the yield of $(\pi\text{-}C_5H_5)_2V(NCS)_2$ was quantitative. *Anal.* Calcd for $C_{12}H_{10}N_2S_2V$: C, 48.5; H, 3.39. Found: C, 48.3; H, 3.30. Infrared bands (cm^{-1}) were observed at 3082 m*, 2062 vs, 2018 vs, 1444 m*, 1429 m*, 837 vs*, 480 vvw, 458 vvw, 408 vw, and 376 vw.

Bis(cyclopentadienyl)vanadium Diselenocyanate, $(\pi\text{-}C_5H_5)_2V(NCSe)_2$.—A solution of KNCSe (4.3 g, 0.03 mol) in 100 ml of a 1:1 v/v acetone–ether mixture was added to $(\pi\text{-}C_5H_5)_2VCl_2$ (2 g, 0.008 mol). The mixture was refluxed for several minutes and then cooled to −70°. The solution was filtered, and the green-brown solid was collected on a frit and washed with water and then ether giving 2.5 g (80%) of $(\pi\text{-}C_5H_5)_2V(NCSe)_2$. The compound exploded violently on ignition and could not be analyzed. Infrared bands (cm^{-1}) were observed at 3090 m*, b, 2083 vw, 2065 vw, 1440 m*, 1425 m*, 1020 w*, 1000 w*, 834 s*, and 829 s .

2,4-Pentanedionatobis(cyclopentadienyl)vanadium(IV) Perchlorate, $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$.—A solution containing $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$ was prepared by adding a slight excess of $AgClO_4$ to a suspension of $(\pi\text{-}C_5H_5)_2VCl_2$ (2.51 g, 0.01 mol) in 75 ml of water and filtering off the precipitated AgCl. Acetylacetone (5 g, 0.05 mol) was added to the filtrate, and the olive green precipitate which formed almost immediately was collected on a frit and washed several times with water and ether giving 3.7 g (96%) of $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$. The compound is extremely explosive and all of the perchlorates should be handled with great care. *Anal.* Calcd for $C_{15}H_{17}ClO_6$: C, 47.4; H, 4.51; Cl, 9.34. Found: C, 48.8; H, 5.13; Cl, 9.56.

2,4-Pentanedionato-d_7-bis(cyclopentadienyl)vanadium(IV) Perchlorate, $[(\pi\text{-}C_5H_5)_2V(C_5D_7O_2)]ClO_4$.—Acetylacetone was deuterated by refluxing 10 ml of acetylacetone, 0.5 g of K_2CO_3, and 100 ml of D_2O for 20 hr. The solution was extracted with three 75-ml portions of ether, the ether was evaporated, and the residue was recycled with fresh D_2O for a total of three times. The deuterated acetylacetone was then treated with a solution of $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$ in D_2O forming olive green $[(\pi\text{-}C_5H_5)_2V(C_5D_7O_2)]ClO_4$. This compound could not be analyzed because of its extremely explosive nature.

2,4-Pentanedionatobis(cyclopentadienyl)vanadium(IV) Trifluoromethylsulfonate, $[(\pi\text{-}C_5H_5)_2V(acac)]F_3CSO_3$.—This green compound was prepared in the same manner as the perchlorate using AgF_3CSO_3 and was thermally stable. *Anal.* Calcd for $C_{10}H_{17}F_3O_5SV$: C, 44.8; H, 3.99; F, 13.3. Found: C, 44.7; H, 4.13; F, 13.2.

Synthesis of Other 2,4-Pentadionatobis(cyclopentadienyl)-vanadium(IV) Salts.—Compounds of the general type $[(\pi\text{-}C_5H_5)_2V(acac)]X^-$, where X^- is a large uninegative anion like BF_4^-, $(C_6H_5)_4B^-$, PF_6^-, $Cl_3CSO_3^-$, I^-, NCS^-, or $NCSe^-$, as well as perchlorate or trifluoromethylsulfonate, could be prepared easily from $(\pi\text{-}C_5H_5)_2VCl_2$ in the following manner. A solution of $[(\pi\text{-}C_5H_5)_2V(acac)]Cl$ was prepared by adding an excess of acetylacetone to a stirred suspension of $(\pi\text{-}C_5H_5)_2VCl_2$ in water. After stirring for *ca.* 30 min, the solution was filtered and a concentrated solution containing the appropriate anion (usually as the sodium or potassium salt) was added to the filtrate. Precipitates of the olive green $(\pi\text{-}C_5H_5)_2V(acac)^+$ salts formed almost instantaneously. These were collected on a frit and washed with water and ethanol. No solid compounds of this type could be obtained when the anion used was NO_3^-, NO_2^-, Br^-, IO_3^-, BrO_3^-, ClO_3^-, NCO^-, $H_3CO_2^-$, $SO_3NH_2^-$, $H_3CSO_3^-$, or any of several dinegative anions including SO_4^{2-}, CrO_4^{2-}, $C_2O_4^{2-}$, and $O_2CCH_2CO_2^{2-}$.

1-Phenyl-1,3-butanedionatobis(cyclopentadienyl)vanadium(IV) Perchlorate, $[(\pi\text{-}C_5H_5)_2V(bzac)]ClO_4$.—A solution of benzoylacetone (0.81 g, 0.005 mol) dissolved in 20 ml of THF was added to 20 ml of an aqueous solution containing 0.002 mol of $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$. The golden-brown crystals which formed on standing overnight were collected on a frit and washed with water and ether giving 0.53 g (60%) of $[(\pi\text{-}C_5H_5)_2V(bzac)]ClO_4$. *Anal.* Calcd for $C_{20}H_{19}ClO_6V$: C, 54.4; H, 4.33; Cl, 8.03. Found: C, 54.1; H, 4.97; Cl, 8.00. Infrared bands (cm^{-1}) were observed at 3110 m*, 1586 s, 1547 s, 1507 vs, 1484 s, 1446 s*, 1431 m, 1368 w, 1350 s, 1305 m, 1293 w, 1203 w, 1177 w, 1158 w, 1104 vs**, 1081 sh, 1063 s, 1023 m, 1011 m, 995 w, 960 w, 928 vw, 843 s*, 759 m, 699 m, 686 w, 676 m, 623 s**, 590 m, 559 m, 438 m, and 378 w. (A double asterisk indicates ClO_4^- vibrations.)

1,3-Diphenyl-1,3-propanedionatobis(cyclopentadienyl)vanadium(IV) Perchlorate, $[(\pi\text{-}C_5H_5)_2V(dbzm)]ClO_4$.—Dibenzoylmethane (0.90 g, 0.004 mol) dissolved in 10 ml of THF was added to an aqueous solution of 0.002 mol of $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$. After standing for several hours, brown crystals began to grow from the solution. These were collected on a frit and washed with water and ether; yield 1.5 g, 50%. *Anal.* Calcd for $C_{25}H_{21}ClO_6V$: C, 59.6; H, 4.20; Cl, 7.04. Found: C, 59.7; H, 4.28; Cl, 7.06. Infrared bands (cm^{-1}) were observed at 3114 m*, 3050 vw, 1612 vw, 1592 m, 1583 s, 1508 vs, 1475 vs, 1449 m*, 1438 m, 1365 m, 1352 s, 1310 m, 1225 m, 1186 m, 1157 w, 1096 vs**, 1064 m, 1020 m*, 1013 m, 996 w, 974 w, 940 m, 870 w, 832 s*, 814 w, 797 vw, 779 m, 758 w, 722 s, 703 m, 686 m, 630 m, 622 s**, 572 m, 545 m, 461 m, 444 m, and 354 m.

1,1,1,5,5,5-Hexafluoro-2,4-pentanedionatobis(cyclopentadienyl)vanadium Perchlorate, $[(\pi\text{-}C_5H_5)_2V(hfacac)]ClO_4$.—A solution of hexafluoroacetylacetone (4.8 g, 0.02 mol) in 10 ml of THF was added to an aqueous solution containing 0.002 mol of $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$. The dark green precipitate which formed after a few hours was collected on a frit and washed with large amounts of water and then ether; yield 0.62 g, 64%. *Anal.* Calcd for $C_{15}H_{11}ClF_6O_6V$: C, 36.9; H, 2.27; Cl, 7.27. Found: C, 36.2; H, 2.81; Cl, 7.42. Infrared bands (cm^{-1}) were observed at 3108 s*, 1636 vs, 1585 m, 1554 s, 1513 m, 1441 vs*, 1356 m, 1252 vs, 1218 vs, 1142 s, 1102 vs**, 1063 s, 1029 m, 1010 m*, 962 w, 932 vw, 862 m, 851 m, 836 w*, 814 w, 793 s, 754 w, 743 w, 669 s, 624 m**, 597 m, 528 w, 462 vw, and 345 vw.

2-Hydroxy-2,4,6-cycloheptatriene-1-onatobis(cyclopentadienyl)-vanadium(IV) Perchlorate, $[(\pi\text{-}C_5H_5)_2V(trop)]ClO_4$.—Tropolone (0.61 g, 0.005 mol) dissolved in 10 ml of THF was added to an aqueous solution containing 0.0025 mol of $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$. The deep violet crystals which formed immediately were collected on a frit and washed with large amounts of water and then ether; yield 0.76 g, 75%. *Anal.* Calcd for $C_{17}H_{15}ClO_6V$: C, 50.8; H, 3.76; Cl, 8.83. Found: C, 50.4; H, 3.62; Cl, 9.08. Infrared bands were observed at 3101 w*, 1592 vs, 1573 w, 1521 vs, 1466 w, 1424 vs*, 1411 s, 1355 s, 1346 s, 1257 w, 1231 w, 1213 m, 1096 vs**, 1055 sh, 1021 w*, 1010 w, 966 w, 876 m, 847 m, 797 w, 752 m, 717 m, 620 w**, 555 m, 457 w, and 431 w.

Magnetic Susceptibility.—The magnetic moments were measured using a Gouy balance based on a Varian V-4004 electromagnet. Field strengths of *ca.* 5 and 8 kG were used. Samples were contained in double-compartment tubes designed for relatively small samples. For calibration, $Hg[Co(NCS)_4]$ prepared by the method of Figgis and Nyholm[9] was used.

Conductivity Measurements.—A Leeds and Northrup Model 260418 AC Jones bridge as described by Dike[10] was used for conductivity measurements in purified nitrobenzene. The null at 12 kcps was indicated on an oscilloscope. A Freas cell thermostated at 25.0° was used, and the cell constant was obtained by measuring the resistance of a 0.0200 *M* KCl solution and taking the specific conductance as 0.002768 $ohm^{-1}\ cm^2$.[11]

Electron Spin Resonance Spectra.—The esr spectra were recorded on a Varian E-3 spectrometer at room temperature.

X-Ray Powder Patterns.—The X-ray patterns were obtained with a General Electric XRD-3 diffractometer using copper Kα radiation.

Infrared Spectra.—A Perkin-Elmer 521 spectrometer was used, and the spectra were obtained using the split halocarbon–Nujol

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[9] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[10] P. H. Dike, *Rev. Sci. Instr.*, **2**, 379 (1931).

[11] G. Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, **55**, 1780 (1933).

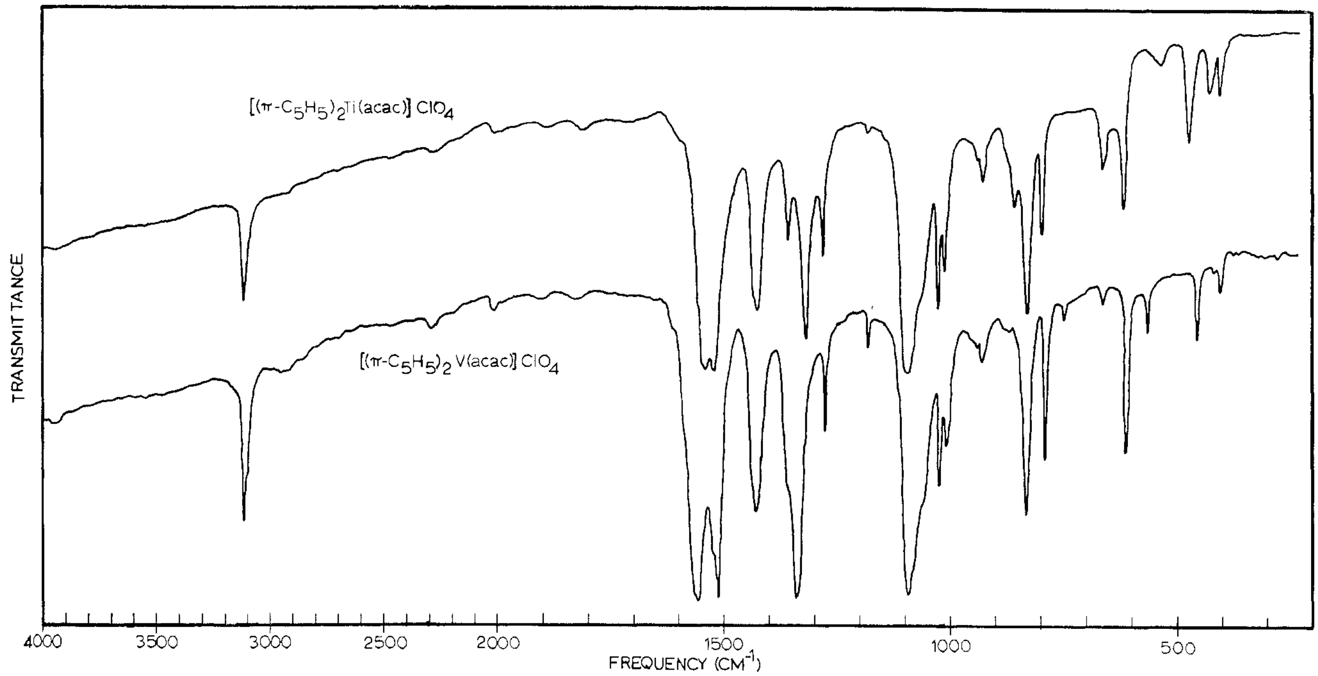

Figure 1.—Infrared spectra of $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$ and $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$.

mull technique with NaCl and CsCl windows. Calibration was effected with polystyrene film.

Results

Infrared Spectra.—The spectrum of $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$ and for comparison the spectrum of $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$ are illustrated in Figure 1. The spectra of these two compounds are almost identical, and the assignment of vibrations mainly localized in the bis(cyclopentadienyl)vanadium(IV) moiety was made easily on the basis of the studies on $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$ and $[(\pi\text{-}C_5D_5)_2Ti(acac)]ClO_4$.[4] The spectra indicate that the acetylacetonate ligand is chelating, and the structures of the complex titanium and vanadium cations must be very similar. The assignments for $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$ and $[(\pi\text{-}C_5H_5)_2V(acac\text{-}d_7)]ClO_4$ are given in Table I.

Table II lists characteristic vibrational frequencies of several other vanadium chelates together with conductivity data. The molar conductivity values are characteristic of 1:1 electrolytes where the values are generally in the range 22–34 ohm^{-1} cm^2.[12]

The molar susceptibility of $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$ was determined to be 1190×10^{-6} cgsu. The diamagnetic correction of 92×10^{-6} cgsu was obtained by measuring the susceptibility of $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$, and the effective magnetic moment was calculated to be 1.74 BM. Because the Gouy method required macrosamples and most of the compounds were extremely explosive, susceptibilities of the other vanadium chelates were not determined.

The esr spectra of several of the vanadium(IV) compounds were obtained, and the data are summarized in Table III. All of the solution spectra show the characteristic eight-line pattern resulting from splitting by the vanadium-51 nucleus. The $\langle g \rangle$ and $\langle a \rangle$ values for

TABLE I

INFRARED SPECTRA OF $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$ AND $[(\pi\text{-}C_5H_5)_2V(acac\text{-}d_7)]ClO_4$

ν, cm^{-1}		
$[(\pi\text{-}C_5H_5)_2V(C_5H_7O_2)]ClO_4$	$[(\pi\text{-}C_5H_5)_2V(C_5D_7O_2)]ClO_4$	Assignment
3116 m	3112 m	(π-Cp)[a] C–H str
1559 vs	1544 vs	(acac) C–O str
1515 vs	1474 s	(acac) C–C str
...	1440 m	(π-Cp) ring str
1433 s	1344 m	(acac) C–C str + CH_3 def
1360 sh	1364 w	(π-Cp) ring str
1342 s	...	(acac) C–O str
1283 m	1236 w	(acac) C–C str + C–CH_3 str
1189 w	790 w	(acac) in-plane C–H bend
1098 vs	1096 vs	(ClO_4^-) ν_3
1032 m	947 w	(acac) CH_3 rock
1016 m	1016 w	(π-Cp) C–H def
935 w	887 w	(acac) C–CH_3 str + C–O str
870 w	870 w	(π-Cp) C–H out-of-plane def
840 s	838 s	(π-Cp) out-of-plane def
800 m	607 w	(acac) C–H out-of-plane def
670 w	...	(acac) ring def
623 m	623 m	$(ClO_4)\nu_4$
576 w	541 w	(acac) C–H out-of-plane def
465 m	450 w	(V–O) str
415 w	380 w	(acac) out-of-plane def

[a] Cp = C_5H_5. [b] s, strong; m, medium; w, weak; v, very; sh, shoulder.

TABLE II

INFRARED AND CONDUCTANCE DATA FOR SEVERAL BIS(CYCLOPENTADIENYL)VANADIUM(IV) COMPOUNDS

	ν, cm^{-1}					
	π-C_5H_5 ring		ClO_4^-		Molar conductivity	
Compound	C–H str	Out-of plane def	ν_3	ν_4	Ohm^{-1} cm^2	Concn, M
$[(\pi\text{-}Cp)_2V(acac)]ClO_4$	3116 m	840 s	1098 vs	623 m	33.6	0.00076
$[(\pi\text{-}Cp)_2V(bzac)]ClO_4$	3110 m	843 s	1104 vs	623 s	32.6	0.00050
$[(\pi\text{-}Cp)_2V(dbzm)]ClO_4$	3114 m	832 s	1096 vs	622 s	29.4	0.00083
$[(\pi\text{-}Cp)_2V(trop)]ClO_4$	3101 w	847 m	1096 vs	620 w	36.7	0.00039
$[(\pi\text{-}Cp)_2V(hfacac)]ClO_4$	3108 s	851 m	1102 vs	624 m	36.0	0.00055
$(\pi\text{-}Cp)_2VCl_2$	3088 m	822 s	...	...	...	...

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(12) C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 4375 (1956).

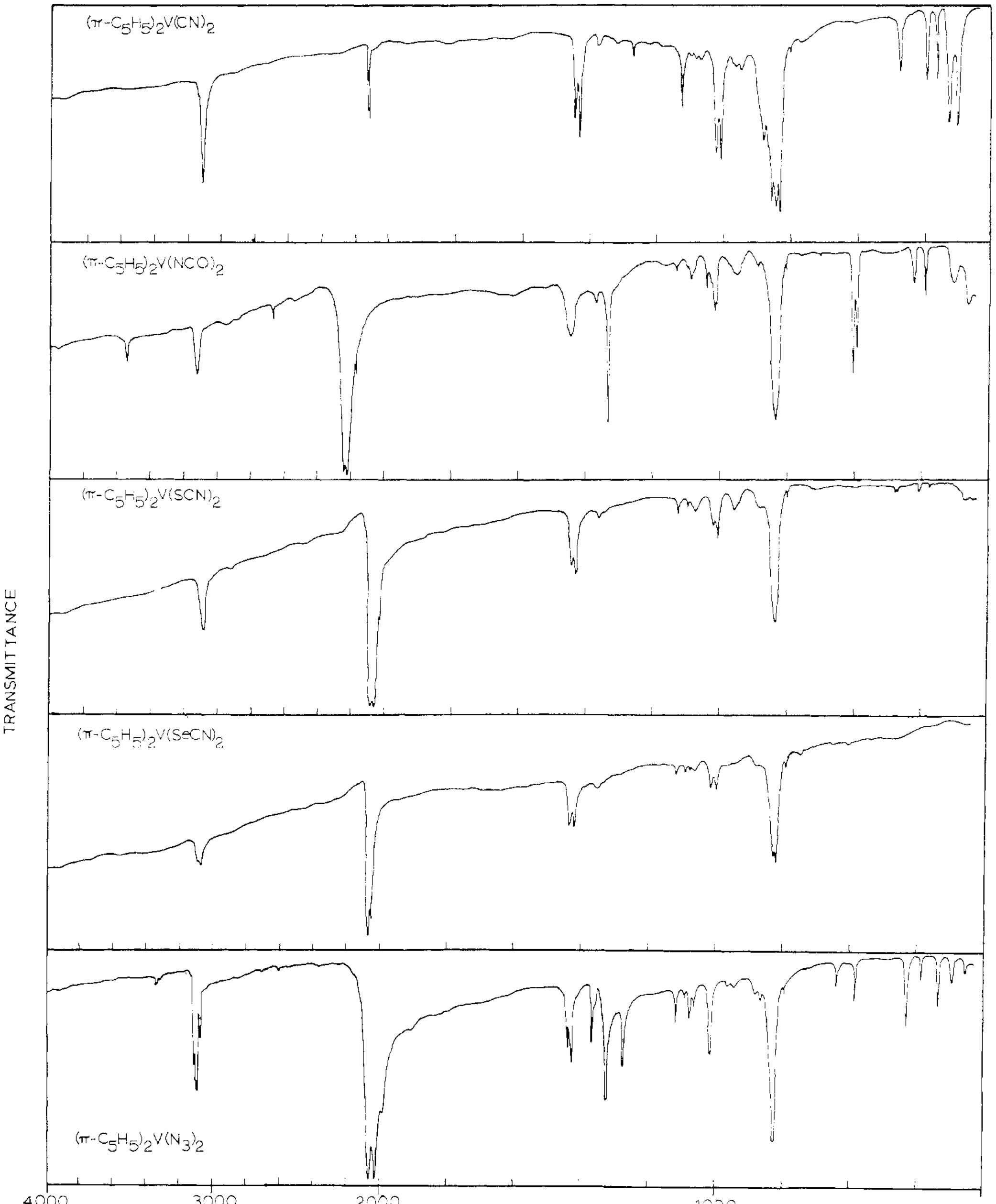

Figure 2.—Infrared spectra of the bis(cyclopentadienyl)vanadium(IV) pseudohalides.

Table III

Electron Spin Resonance Data for Some Bis(cyclopentadienyl)vanadium(IV) Compounds at ~300°K in Chloroform Solution

Compound	⟨g⟩	⟨a⟩, G
$[(\pi\text{-Cp})_2V(\text{trop})]ClO_4$	1.983	65.9
$[(\pi\text{-Cp})_2V(\text{bdzm})]ClO_4$	1.985	74.6
$(\pi\text{-Cp})_2VCl_2$	1.988	74.3
$(\pi\text{-Cp})_2V(N_3)_2$	1.985	72.0
$(\pi\text{-Cp})_2V(CN)_2$	1.999	60.3
$(\pi\text{-Cp})_2V(NCO)_2$	1.985	76.1
$(\pi\text{-Cp})_2V(NCS)_2$	1.991	73.0
$(\pi\text{-Cp})_2V(NCSe)_2$	1.990	73.6

these second-order spectra were calculated using the relations given by Rogers and Pake.[13] No spectra could be obtained from chloroform solutions of $[(\pi\text{-}C_5H_5)_2V(\text{bzac})]ClO_4$ or $[(\pi\text{-}C_5H_5)_2V(\text{acac})]ClO_4$ at room temperature.

X-Ray powder patterns were determined for both $[(\pi\text{-}C_5H_5)_2V(\text{acac})]ClO_4$ and its titanium analog, $[(\pi\text{-}C_5H_5)_2Ti(\text{acac})]ClO_4$. Intense reflections were observed at the following values of 2θ (value for vanadium compound given first): 17.3, 17.4; 18.9, 18.7; 23.8, 23.6; 27.7, 27.7; 30.0, 30.0; 32.3, 32.3; 34.6, 34.3; 38.7, 38.4; 44.7, 44.6; 65.2, 65.1°.

Discussion

The behavior of the bis(cyclopentadienyl)vanadium(IV) moiety appears to parallel that of the bis(cyclopentadienyl)titanium(IV) analog almost exactly in its reactions with most ligands. Thus β-diketonate chelates of the $(\pi\text{-}C_5H_5)_2V^{IV}$ moiety and the conjugate bases of acetylacetone, benzoylacetone, dibenzoylmethane, and tropolone could all be prepared by the reaction of

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[13] R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, **3**, 1107 (1960).

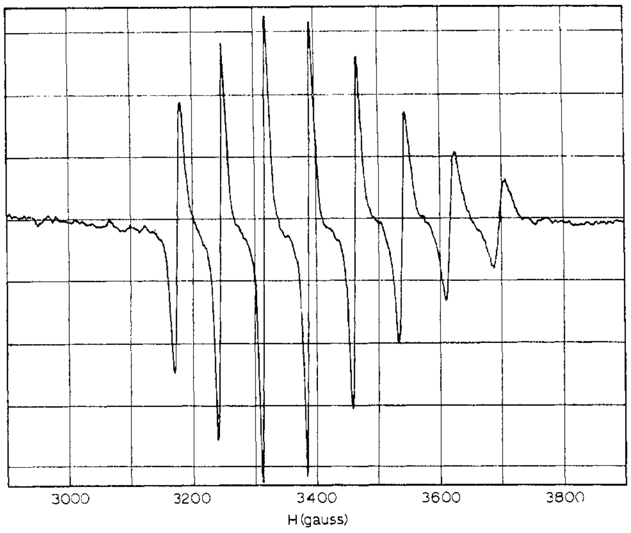

Figure 3.—Esr spectrum of $[(\pi\text{-}C_5H_5)_2V(dbzm)]ClO_4$ in chloroform solution at ~300°K.

aqueous $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$ with the free β-diketone in reactions analogous to those of the corresponding titanium compound. It is probable that the reactions involve a hydroxy intermediate, *i.e.*

$$2AgClO_4 + (\pi\text{-}C_5H_5)_2VCl_2 \xrightarrow{H_2O} (\pi\text{-}C_5H_5)_2VOH^+ + H_3O^+ + \underline{2AgCl} + 2ClO_4^-$$

$$ClO_4^- + (\pi\text{-}C_5H_5)_2VOH^+ + HL \xrightarrow{H_2O} \underline{[(\pi\text{-}C_5H_5)_2VL]^+ClO_4^-} + H_2O$$

However, no work has been reported on the hydrolysis of the bis(cyclopentadienyl)vanadium(IV) cation. Surprisingly, no complex could be obtained with dipivaloylmethane, although the titanium compound has been prepared.[4] After 8 days of stirring $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$ with dipivaloylmethane in a water–THF solution, the unreacted ligand could be recovered quantitatively. It was also possible to prepare the acetylacetonate chelate by the reaction of $(\pi\text{-}C_5H_5)_2VCl_2$, Hacac, and $NaClO_4$ in aqueous solution as was used for the titanium chelate.

In the case of acetylacetonate derivatives $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$ and $[(\pi\text{-}C_5H_5)_2Ti(acac)]ClO_4$, the details of the structures must be essentially the same. The infrared spectra of the two compounds are almost identical. The molar conductivity in dilute solution of the titanium compound was 31.6 while that of the vanadium analog was 33.6 ohm^{-1} cm.[2] The X-ray powder patterns indicate that the crystals of the two compounds are isomorphous.

The bulk magnetic susceptibility measurement on $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$ gave a value of $\mu_{eff} = 1.74$ BM. As expected because of the low ionic symmetry, this is very close to the spin-only value for one unpaired electron. The $\langle g \rangle$ values determined from the esr spectra are all essentially the free-electron value. Both the values for $\langle g \rangle$ and $\langle a \rangle$ obtained for $(\pi\text{-}C_5H_5)_2VCl_2$ are in good agreement with those obtained previously.[14] The invariance of the hyperfine constant $\langle a \rangle$ as the ligands about $(\pi\text{-}C_5H_5)_2V^{IV}$ are changed indicates that the single unpaired electron is in an orbital essentially localized on the vanadium atom. This is in agreement with the type of bonding suggested for the titanium chelates.[4] The nonbonding orbital constructed from the metal s and one p orbital[15] which is vacant in the titanium(IV) chelate would then accommodate the unpaired electron in the vanadium(IV) compound.

An attempt was made to synthesize the chelate with acetylacetonate imide to determine if the unpaired electron were delocalized at all into the ring system. Reaction of $(\pi\text{-}C_5H_5)_2VCl_2$, $AgClO_4$, and acetylacetone imide in an aqueous system gave only $[(\pi\text{-}C_5H_5)_2V(acac)]ClO_4$. Under anhydrous conditions, the only solid product which could be isolated was NH_4ClO_4. There was no evidence, however, of any interaction with the nitrogen nuclei in the azide.

It is surprising that it proved impossible, presumably because of very broad lines, to observe esr spectra for the compounds with acetylacetonate or benzoylacetonate as the ligands. There is no reason to expect shorter relaxation times with these ligands than, *e.g.*, with the conjugate base of dibenzoylmethane, and it may result from clustering of the ions with the less bulky ligands in the $CHCl_3$ solution. The hyperfine splitting constant was reported to be 210 Mcps for the oxidation product of $(\pi\text{-}C_5H_5)_2V$, and this has been described as a vanadyl complex, $(\pi\text{-}C_5H_5)_2VO$.[16] This is similar to the value for the dibenzoylmethanato complex (74.6 G = 209 Mcps) suggesting that the oxidation product probably has a similar structure and consequently may be $(\pi\text{-}C_5H_5)_2V(OH)_2$.

No pmr spectra could be obtained for the paramagnetic vanadium(IV) compounds. This is not surprising, since the electronic relaxation times are sufficiently long for most of the compounds to give sharp esr signals at room temperature. The behavior is much like that of vanadyl acetylacetonate.[17] With the acetylacetonate in dimethylformamide, the signals were broadened to the extent that the usual doublet for the methyl protons of the solvent could not be resolved and the line width for the TMS standard was greater than 20 cps. In addition, the highest concentrations of solute which could be attained were *ca.* 0.1 *M*, adding to the difficulty of detecting very broad signals.

The chelates with these oxygen donors are easily synthesized and are quite stable except when perchlorate is the anion when they tend to detonate. It seems likely that this ease of precipitation from solution results, primarily, from very low hydration energies for the large cations which leads to very slightly water-soluble compounds with large uninegative anions.

The pseudohalide complexes are stable to water and in some cases can be precipitated from aqueous solution indicating that reaction to form V–O bonds is not favored. The cyanate shows an intense infrared

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[14] J. C. W. Chien and C. R. Boss, *J. Am. Chem. Soc.*, **83**, 3767 (1961).

[15] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

[16] H. N. McConnell, W. W. Porterfield, and R. E. Robertson, *J. Chem. Phys.*, **30**, 442 (1959).

[17] D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

band at 1329 cm^{-1}, and this is consistent with an isocyanate structure.[18] Bis(cyclopentadienyl)titanium(IV) dicyanate also was assigned the isocyanate structure on the basis of the presence of two infrared bands at 1300 and 1370 cm^{-1}.[19] It is not possible to state with confidence whether the thiocyanate and selenocyanate are bound through nitrogen or the group VI atom. Coutts and Wailes[19] have suggested that the titanium compound $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$ is nitrogen bonded because of the absence of an infrared band in the region 650–800 cm^{-1}. The spectrum of the vanadium analog is similar. On the other hand Giddings[20] suggests bonding through sulfur for the titanium compound and classifies the bis(cyclopentadienyl)titanium(IV) moiety as a soft acid because of its ease of reaction with thiols compared to alcohols. With bis(cyclopentadienyl)vanadium(IV), the stability of the cyanate and azide make the isothiocyanate and isoselenocyanate structures plausible. Although much effort has been made to determine the mode of attachment of SCN^- and $SeCN^-$ from vibrational spectra, these questions cannot be settled with any degree of confidence on the basis of infrared data alone, especially when the low-frequency vibrations occur with very low intensity as is the case here.

Acknowledgments.—Financial support to G. D. in the form of Du Pont and NSF summer fellowships is gratefully acknowledged.

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[18] See the discussion by J. S. Thayer and R. West, *Advan. Organometal. Chem.*, **5**, 115 (1967).

[19] R. S. P. Coutts and P. C. Wailes, *Australian J. Chem.*, **19**, 2069 (1966).

[20] S. A. Giddings, *Inorg. Chem.*, **6**, 849 (1967).

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Isolation of Complex Halogeno Anions as the Acetylacetonatobis(cyclopentadienyl)titanium(IV) and -vanadium(IV) Salts. Reactions of $(\pi\text{-}C_5H_5)_2Ti^{IV}$ and $(\pi\text{-}C_5H_5)_2V^{IV}$ with Squarate and Ethyl Acetoacetate Ions[1,2]

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The complex anions $FeCl_4^-$, $CoCl_4^{2-}$, $ZnCl_3(H_2O)^-$, $SnCl_3^-$, $CdCl_4^{2-}$, and $SnCl_6^{2-}$ have been precipitated from aqueous solutions of the metal chlorides in the presence of excess chloride ion by the cations $(\pi\text{-}C_5H_5)_2Ti(acac)^+$ and $(\pi\text{-}C_5H_5)_2V(acac)^+$. Conductivity measurements indicate that these compounds are all electrolytes in nitrobenzene solution. Reaction of $(\pi\text{-}C_5H_5)_2Ti^{IV}$ with the squarate ion, $C_4O_4^{2-}$, gives a compound where squarate appears to function as a simple bidentate ligand behaving much like tropolonate. Reactions of $(\pi\text{-}C_5H_5)_2Ti(ClO_4)_2$ and $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$ with ethyl acteoacetate give complexes of the type $[(\pi\text{-}C_5H_5)_2M(C_6H_9O_3)]ClO_4$, M = Ti and V. In the vanadium compound the ethyl acetoacetate ligand is chelated normally, while the titanium analog appears to involve coordination *via* one keto oxygen and the "ether" oxygen.

Introduction

In previous communications we have described reactions in aqueous solution of $(\pi\text{-}C_5H_5)_2Ti(ClO_4)_2$[4] and $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$[5] with bidentate ligands. Very slightly soluble compounds of the type $[(\pi\text{-}C_5H_5)_2ML]ClO_4$ were obtained where M = Ti(IV) or V(IV) and L is the conjugate base of acetylacetone, benzoylacetone, dibenzoylmethane, and tropolone. Analogous salts were obtained when perchlorate was replaced by other large uninegative anions like BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, $F_3CSO_3^-$, $Cl_3CSO_3^-$, $(C_6H_5)_4B^-$, I^-, NCS^-, and $NCSe^-$.

It was only possible to coordinate one bidentate ligand to the bis(cyclopentadienyl)titanium(IV) or -vanadium(IV) moiety, and it was suggested that the ease of preparation of these mono-β-diketonate complexes resulted from the very low solvation energy of the complex cation. This suggested that many uninegative complex halogeno anions present in aqueous solution might be isolated as salts of these large cations. This communication describes the isolation of a number of such chloro complexes.

Although there is a very close parallel between the reaction of analogous bis(cyclopentadienyl)titanium(IV) and -vanadium(IV) compounds, the reaction with ethyl acetoacetate is one case where different products are obtained. Structures are suggested for these two compounds.

In an effort to force the coordination of more than two oxygen atoms about the bis(cyclopentadienyl)titanium(IV) moiety, the squarate complex was synthesized. Several compounds of the type $M(C_4O_4)\cdot 2H_2O$ with dipositive transition metal cations have been prepared, and it has been suggested that they have a

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[1] Supported, in part, by the National Science Foundation, Grant GP-5022.

[2] Taken from a thesis submitted by G. D. to the Graduate School of the University of Minnesota for the Ph.D. degree, 1967.

[3] NASA Trainee, 1965–1967.

[4] G. Doyle and R. S. Tobias, *Inorg. Chem.*, **6**, 1111 (1967).

[5] G. Doyle and R. S. Tobias, *ibid.*, **7**, 2479 (1968).