Electron Paramagnetic Resonance Spectra of the Bis-(π-cyclopentadienyl)vanadium(IV) and Bis-(π-cyclopentadienyl)niobium(IV) Complexes $(\pi\text{-}C_5H_5)_2VX_2$ and $(\pi\text{-}C_5H_5)_2NbX_2$

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X-Band e.p.r. spectra of magnetically dilute glasses containing $(\pi\text{-}C_5H_5)_2VX_2$ and $(\pi\text{-}C_5H_5)_2NbX_2$ (X = Cl, SCN, OCN, and CN) have been recorded at 77 and 290 K and are analysed in detail. The metal-ion spin–orbit coupling constants, ξ_V and ξ_{Nb}, for these molecules are estimated to be +133 and +490 cm^{-1} respectively. Spin Hamiltonian parameters are listed for each substance and are equated to the atomic orbital coefficients in some of the molecular orbitals involved in bonding in these molecules. Except for the cyanides, in each case the unpaired electron lies essentially in a non-bonding nd_{z^2} metal-ion orbital mixed with a small amount of the corresponding metal ion $nd_{x^2-y^2}$ orbital, the z-axis coinciding with the C_2 axis of the compound; in the cyanides this unpaired electron is delocalised into p_x orbitals on the ligands. π-Electrons of the cyclopentadienide rings and σ-bonding electrons derived from the other ligands X are almost completely delocalised, π-bonding to the cyclopentadienide residues being stronger than σ-bonding to the ligands X. Several redistribution complexes $(\pi\text{-}C_5H_5)_2NbXY$ have been detected. E.p.r. techniques can be used to distinguish compounds of the type $(\pi\text{-}C_5H_5)_2MX_2$ from other compounds which contain vanadium(IV) or niobium(IV). Hückel LCAO molecular orbital calculations carried out on these molecules appear to give reasonable descriptions of their ground states.

ELECTRON PARAMAGNETIC RESONANCE (e.p.r.) methods have been widely used to obtain detailed information about electron distributions in transition-metal ion complexes in paramagnetic salts; the paramagnetic resonance properties of the $3d^1$ oxovanadium(IV) ion have been particularly exhaustively studied in this way. In tetrahedral complexes, ligand-field splitting of nd basis states is opposite in sign from, and is usually smaller than, the splitting encountered in corresponding tetragonally distorted octahedral complexes; furthermore, the tetrahedron does not have a centre of inversion and so metal ion d orbitals can then be mixed with orbitals of opposite parity, for example with metal ion $(n+1)p$ orbitals. This hybridisation, along with differences in the degree of covalent bonding to neighbouring ligands causes spin–orbit coupling and hyperfine interactions in tetrahedral species to be noticeably different from the corresponding interactions in octahedral complexes.[1-4]

Tetrahedral complexes containing vanadium(IV) and niobium(IV) are rather uncommon. The only magnetically dilute systems for which detailed analyses of the e.p.r. properties of vanadium(IV) in a tetrahedral environment appear to have been made are the chloride,[5] alkoxide,[6-8] and amino[7-9] derivatives, VCl_4, $V(OBu^t)_4$, and $V(NR_2)_4$, where in each case the unpaired electron lies essentially in the $3d_{x^2-y^2}$ orbital of the vanadium ions.

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Other than niobium doped into a molybdenum sulphide host lattice,[10] the only magnetically dilute complexes containing niobium(IV) in a tetrahedral environment that appear to have been studied in detail are the amino-derivatives $Nb(NR_2)_4$,[11] although magnetic susceptibility measurements and isotropic solution e.p.r. data have been reported for several axially distorted bis-(π-cyclopentadienyl) derivatives $(\pi\text{-}C_5H_5)_2MX_2$, ($M = V^{IV}$ and and Nb^{IV}).[12-16] Here we report e.p.r. spectra obtained from glasses which contain distorted metallocene derivatives of this type and discuss the conclusions which can be drawn about electron distributions within these molecules when such spectra are analysed in detail.

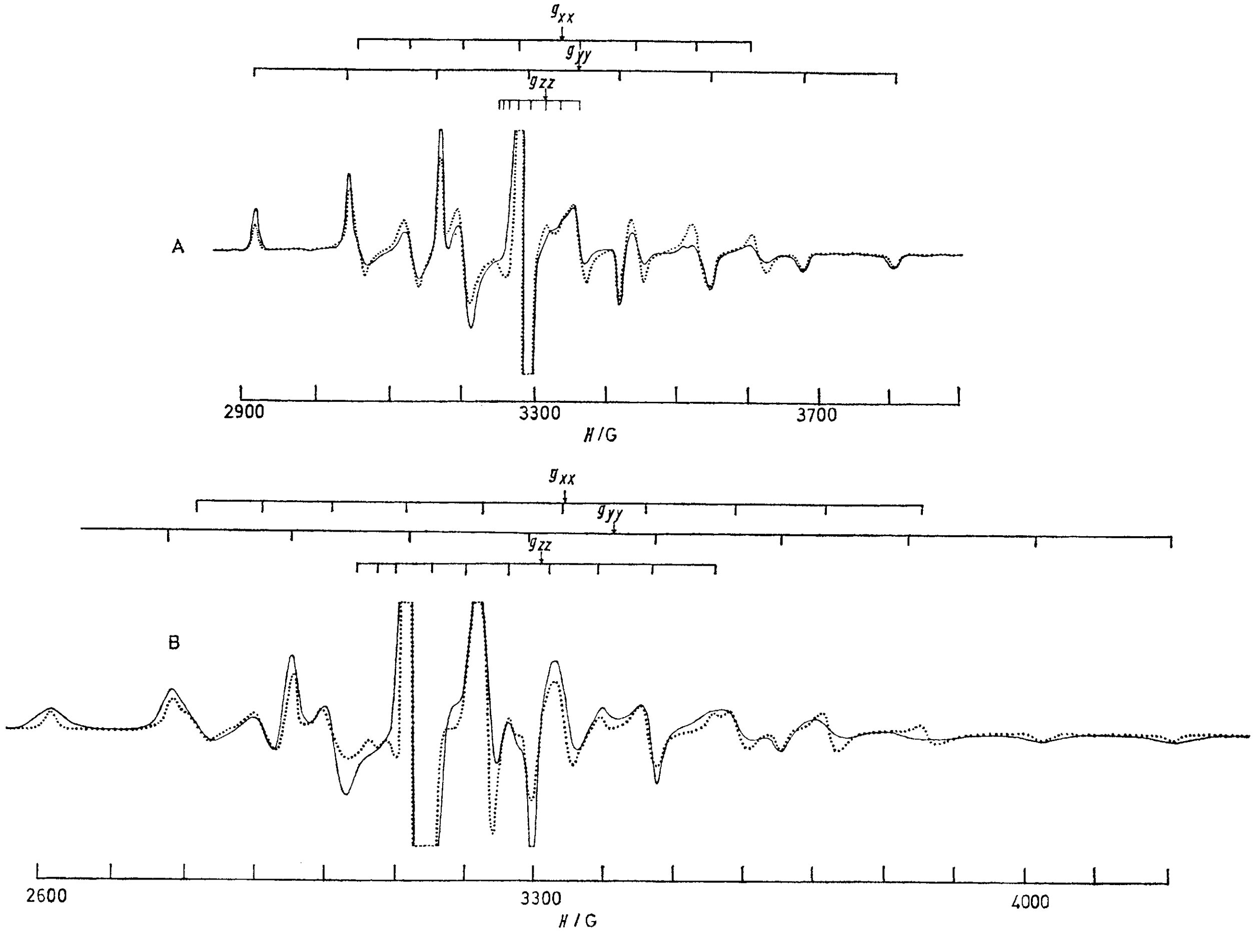

FIGURE 1 Observed (——) and calculated (· · · ·) e.p.r. spectra of 10^{-3}M-solutions of $(\pi\text{-}C_5H_5)_2VCl_2$, A, and of $(\pi\text{-}C_5H_5)NbCl_2$, B, in $CHCl_3$–EtOH glass (9 : 1) at 77 K

EXPERIMENTAL

Dichlorobis-(π-cyclopentadienyl)vanadium(IV), $(\pi\text{-}C_5H_5)_2VCl_2$, was prepared by allowing vanadium tetrachloride to react with sodium cyclopentadienide in diglyme solution.[12,17] The corresponding dithiocyanate, dicyanate, and dicyanide, were then prepared from the dichloride by appropriate reaction with KSCN, KOCN, and KCN respectively.[15] Tetracyclopentadienylniobium(IV), $(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2$, was prepared by allowing niobium pentachloride to react with a suspension of sodium cyclopentadienide in benzene.[14,16,18] Dichlorobis-(π-cyclopentadienyl)niobium(IV), $(\pi\text{-}C_5H_5)_2NbCl_2$, was then prepared by treating the $(C_5H_5)_4Nb$ with a saturated solution of dry hydrogen chloride in ether.[16,18] The corresponding dithiocyanate, $(\pi\text{-}C_5H_5)_2Nb(SCN)_2$, and dicyanide, $(\pi\text{-}C_5H_5)_2Nb(CN)_2$, were prepared by stirring a solution of the dichloride with KSCN or KCN in dimethylformamide, for 1 and 4 h respectively.

With the exception of $(C_5H_5)_4Nb$, thoroughly out-gassed 10^{-3}M-solutions of each of the above compounds in chloroform containing 10% of ethanol were examined at 290 and 77 K in a Decca X3 spectrometer combined with a Newport Instruments 11-in magnet system. All resonance fields

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were calibrated by standard proton magnetic resonance techniques. The complex $(C_5H_5)_4Nb$ is unstable in solutions which contain ethanol and so its spectra were recorded in toluene. Typical e.p.r. spectra recorded at 77 K are shown in Figure 1. We have found that replacement of the σ-bonded ligands in $(\pi\text{-}C_5H_5)_2NbCl_2$ occurs sufficiently slowly to enable ligand-exchange reactions to be monitored in the e.p.r. spectrometer and, although they have not been isolated, e.p.r. spectra of the redistribution complexes $(\pi\text{-}C_5H_5)_2NbCl(SCN)$, $(\pi\text{-}C_5H_5)_2NbCl(\sigma\text{-}C_5H_5)$, and $(\pi\text{-}C_5H_5)_2NbCl(CN)$ have been observed and characterised at 290 K. We have not been able to detect ^{14}N hyperfine coupling in any of these systems.

Visible–u.v. absorption spectra of dichloromethane solutions, and also, where possible, of dimethylformamide solutions of most of the above complexes were recorded on Unicam SP 700C and 800 spectrophotometers, using matched 1-cm quartz cells; $\nu_{max.}$ values are listed in Table 1.

TABLE 1

Band maxima (cm^{-1}) in the visible–u.v. absorption spectra of the metallocene derivatives $(\pi\text{-}C_5H_5)_2VX_2$ and $(\pi\text{-}C_5H_5)_2NbX_2$. Rapid decomposition prevented some data from being obtained in *

Compound	$d \leftarrow d$ Transition	Metal ion $\leftarrow$ ring charge transfer	Other bands
$(\pi\text{-}C_5H_5)_2VCl_2$	11 800 13 600	26 300	35 400
$(\pi\text{-}C_5H_5)_2V(SCN)_2$	14 000	25 000	21 600 28 900 37 800
$(\pi\text{-}C_5H_5)_2V(OCN)_2$	13 300	26 800	36 100
$(\pi C_5H_5)_2V(CN)_2$	16 900	25 000	32 700 40 000
$(\pi\text{-}C_5H_5)_2NbCl_2$	14 500 17 000 20 400	28 500	41 000
$(\pi\text{-}C_5H_5)_2Nb(SCN)_2$	17 000	27 500	22 600; 38 500
$(\pi\text{-}C_5H_5)_2Nb(CN)_2$	20 300	29 800	*

These spectra are all very much alike and they can be explained qualitatively in the following way. (i) They all exhibit broad, weak absorption bands in the 10 000—20 000 cm^{-1} region which are ascribed to $d \leftarrow d$ transitions; additional structure in this region of the spectrum could only be resolved in the case of the chlorides $(\pi\text{-}C_5H_5)_2VCl_2$ and $(\pi\text{-}C_5H_5)_2NbCl_2$.[19,20] (ii) Spectra of the vanadium(IV) complexes all show intense charge-transfer bands at *ca.* 26 000 cm^{-1} and the niobium(IV) complexes at *ca.* 28 000 cm^{-1}. These are assigned to transitions in which an electron transfers from an orbital, which is essentially a cyclopentadienide ring molecular orbital, to that orbital which contains the unpaired electron. These are metal ion$\leftarrow$ring charge-transfer bands and therefore their frequencies are essentially independent of the nature of the σ-bonded ligands. (iii) In each complex, additional, intense, unassigned absorption bands occur at higher frequencies. In the thiocyanato-complexes an additional strong absorption band is found at *ca.* 22 000 cm^{-1}; this is assigned to the internal $\pi^* \leftarrow \pi$ transition of the thiocyanato-residues.[21] (iv) The $d \leftarrow d$ transitions of $(\pi\text{-}C_5H_5)_4Nb$ are masked by very intense absorption which may be due to charge transfer from the central metal ion to the π^* orbitals of the $(\sigma\text{-}C_5H_5)$ residues.

Analysis of E.p.r. Spectra.—In analysing spectra of these d^1 complexes of vanadium(IV) and niobium(IV) it has been assumed that they all have C_{2v} symmetry and since the analyses subsequently showed that quadrupolar and Zeeman interactions at the central metal ion nuclei are very weak in these species the spin-Hamiltonian used was the standard diagonal form:

$$\mathscr{H} = \beta_e[g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_zS_z] + T_{xx}I_xS_x + T_{yy}I_yS_y + T_{zz}I_zS_z \quad (1)$$

Spectra obtained from glasses of the vanadium series at 77 K were analysed using methods already described,[22] and the spectra of the niobium(IV) compounds (^{93}Nb, natural abundance 100%, $I = 9/2$) were fitted to similar curves of the form

$$F(H') = (2\pi)^{-\frac{1}{2}} \sum_{m_I = -9/2}^{m_I = +9/2} \int_{H=-\infty}^{+\infty} \beta^{-1}S_{m_I}(H)\exp\,[-(H' - H)^2(2\beta^2)^{-1}]\mathrm{d}H \quad (2)$$

where $S_{m_I}(H)$ is a Kneubühl function [22,23] and β is an appropriate Gaussian broadening factor. Spin-Hamiltonian parameters obtained using these procedures are listed in Table 2 and spectra computed from equation (2) for $(\pi\text{-}C_5H_5)_2NbCl_2$ and from the similar equation appropriate [22] to $(\pi\text{-}C_5H_5)_2VCl_2$ are shown in Figure 1.

RESULTS AND DISCUSSION

Table 2 shows that e.p.r. methods can be used to quickly distinguish these 'tetrahedral' species from 'tetragonal' vanadyl or niobyl complexes, and from other, 'tetrahedral', species in which the unpaired electrons are known to be in molecular orbitals derived from the $d_{x^2-y^2}$ orbitals of the central metal ions.[4-11,22,24] The g-tensor components listed in Table 2 show that in each compound the unpaired electron occupies a molecular orbital which is primarily metal ion d_{z^2} in character, although the marked deviations from cylindrical symmetry in both the g- and T-tensors show that the metal ion $d_{x^2-y^2}$ orbitals also contribute. Analyses of the e.p.r. spectra show that the signs of T_{xx}, T_{yy}, and T_{zz} must be the same. Direct dipolar contributions to T_{zz} can be shown to be positive in these compounds, hence, since in each case $|T_{zz}| < |a'|$, it follows that a' and T_{xx}, T_{yy}, and T_{zz} must all be negative.

More precise information can be obtained about electron distributions within these complexes if their spin Hamiltonian parameters are equated with the coefficients in appropriate linear combinations of atomic orbitals. Using the co-ordinate system of Figure 2, molecular orbitals in this compound may be described in terms of basis orbitals derived from (i), the $3d$, $4s$, and $4p$ orbitals of the central metal ion, (ii), chloride ion p-orbitals, and

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TABLE 2

Spin Hamiltonian parameters for the metallocene derivatives $(\pi\text{-}C_5H_5)_2VXY$ and $(\pi\text{-}C_5H_5)_2NbXY$. All tensor components refer to compounds in chloroform: ethanol (9 : 1) glass at 77 K, except for $\langle g' \rangle$ and $|a'|$ which are the isotropic g-factor and central metal ion hyperfine coupling parameters at 290 K. The redistribution complexes * could only be examined at 290 K. All hyperfine tensor components are in units of cm^{-1}. Limits of errors are g_{xx} and $g_{yy} = \pm 0{\cdot}0005$, $g_{zz} = \pm 0{\cdot}001$, T_{xx}, T_{yy}, and $T_{zz} = \pm 0{\cdot}00002\ cm^{-1}$, except for $(\pi\text{-}C_5H_5)_2VCl_2$ where the limits of error in T_{xx}, T_{yy}, and T_{zz} are $\pm 0{\cdot}00005\ cm^{-1}$

Compound	g_{xx}	g_{yy}	g_{zz}	T_{xx}	T_{yy}	T_{zz}	$\langle g \rangle$	a	$\langle g' \rangle$	$\lvert a' \rvert$
$(\pi\text{-}C_5H_5)_2VCl_2$	1·986	1·971	2·000	−0·00740	−0·01170	−0·00152	1·986	−0·00687	1·988	0·00687
$(\pi\text{-}C_5H_5)_2V(SCN)_2$	1·988	1·958	2·000	−0·00712	−0·01153	−0·00192	1·982	−0·00686	1·986	0·00681
$(\pi\text{-}C_5H_5)_2V(OCN)_2$	1·985	1·957	2·000	−0·00734	−0·01194	−0·00186	1·981	−0·00708	1·980	0·00708
$(\pi\text{-}C_5H_5)_2V(CN)_2$	1·994	1·986	2·000	−0·00587	−0·00991	−0·00110	1·993	−0·00562	1·994	0·00565
$(\pi\text{-}C_5H_5)_2NbCl_2$	1·980	1·940	2·000	−0·01066	−0·01598	−0·00528	1·974	−0·01064	1·976	0·01064
$(\pi\text{-}C_5H_5)_2NbCl(SCN)$					*				1·976	0·01057
$(\pi\text{-}C_5H_5)_2NbCl(\sigma\text{-}C_5H_5)$					*				1·984	0·00982
$(\pi\text{-}C_5H_5)_2NbCl(CN)$					*				1·984	0·00973
$(\pi\text{-}C_5H_5)_2Nb(SCN)_2$	1·987	1·935	2·000	−0·01005	−0·01536	−0·00528	1·975	−0·01023	1·975	0·01027
$(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2$	1·982	1·979	1·999	−0·00908	−0·01431	−0·00437	1·987	−0·00925	1·988	0·00923
$(\pi\text{-}C_5H_5)_2Nb(CN)_2$	1·997	1·976	2·003	−0·00771	−0·01293	−0·00534	1·992	−0·00834	1·995	0·00839

(iii) cyclopentadienide ion molecular orbitals; these last are the linear combinations

$$\mathrm{cp}(1) = \frac{1}{\sqrt{5}}[\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5] = \mathrm{cp}_0$$

$$\left.\begin{aligned} \mathrm{cp}(2) &= \\ &\sqrt{\frac{2}{5}}\left[\phi_1 + \cos\frac{2\pi}{5}(\phi_2+\phi_5) + \cos\frac{4\pi}{5}(\phi_3+\phi_4)\right] \\ \mathrm{cp}(3) &= \sqrt{\frac{2}{5}}\left[\sin\frac{2\pi}{5}(\phi_2-\phi_5) + \sin\frac{4\pi}{5}(\phi_3-\phi_4)\right] \end{aligned}\right\} = \mathrm{cp}_{\pm 1}$$

$$\left.\begin{aligned} \mathrm{cp}(4) &= \\ &\sqrt{\frac{2}{5}}\left[\phi_1 + \cos\frac{4\pi}{5}(\phi_2+\phi_5) + \cos\frac{2\pi}{5}(\phi_3+\phi_4)\right] \\ \mathrm{cp}(5) &= \sqrt{\frac{2}{5}}\left[\sin\frac{4\pi}{5}(\phi_2-\phi_5) - \sin\frac{2\pi}{5}(\phi_3-\phi_4)\right] \end{aligned}\right\} = \mathrm{cp}_{\pm 2}$$

where ϕ_1—ϕ_5 are appropriate p-orbitals of the cyclopentadienide ion. In the C_{2v} group the 25 basis orbitals fall into the following symmetry classes:

Class	A_1	A_2
Metal ion orbitals	$4s;\ 4p_z;\ 3d_{z^2};\ 3d_{x^2-y^2}$	$3d_{xy}$
Chloride ion orbitals	$p_x[A_1] = \frac{1}{\sqrt{2}}[p_{x_A} - p_{x_B}]$ $p_z[A_1] = \frac{1}{\sqrt{2}}[p_{z_A} + p_{z_B}]$	$p_y[A_2] = \frac{1}{\sqrt{2}}[p_{y_A} - p_{y_B}]$
Cyclopentadienide ion orbitals	$\mathrm{cp}_0[A_1] = \frac{1}{\sqrt{2}}[\mathrm{cp}(1)_A + \mathrm{cp}(1)_B]$ $\mathrm{cp}_1[A_1] = \frac{1}{\sqrt{2}}[\mathrm{cp}(2)_A + \mathrm{cp}(2)_B]$ $\mathrm{cp}_2[A_1] = \frac{1}{\sqrt{2}}[\mathrm{cp}(4)_A + \mathrm{cp}(4)_B]$	$\mathrm{cp}_1[A_2] = \frac{1}{\sqrt{2}}[\mathrm{cp}(3)_A - \mathrm{cp}(3)_B]$ $\mathrm{cp}_2[A_2] = \frac{1}{\sqrt{2}}[\mathrm{cp}(5)_A - \mathrm{cp}(5)_B]$

Class	B_1	B_2
Metal ion orbitals	$3d_{xz};\ 4p_x$	$3d_{yz};\ 4p_y$
Chloride ion orbitals	$p_x[B_1] = \frac{1}{\sqrt{2}}[p_{x_A} + p_{x_B}]$ $p_z[B_1] = \frac{1}{\sqrt{2}}[p_{z_A} - p_{z_B}]$	$p_y[B_2] = \frac{1}{\sqrt{2}}[p_{y_A} + p_{y_B}]$
Cyclopentadienide ion orbitals	$\mathrm{cp}_1[B_1] = \frac{1}{\sqrt{2}}[\mathrm{cp}(3)_A + \mathrm{cp}(3)_B]$ $\mathrm{cp}_2[B_1] = \frac{1}{\sqrt{2}}[\mathrm{cp}(5)_A + \mathrm{cp}(5)_B]$	$\mathrm{cp}_0[B_2] = \frac{1}{\sqrt{2}}[\mathrm{cp}(1)_A - \mathrm{cp}(1)_B]$ $\mathrm{cp}_1[B_2] = \frac{1}{\sqrt{2}}[\mathrm{cp}(2)_A - \mathrm{cp}(2)_B]$ $\mathrm{cp}_2[B_2] = \frac{1}{\sqrt{2}}[\mathrm{cp}(4)_A - \mathrm{cp}(4)_B]$

Standard Hückel calculations carried out on linear combinations of orbitals belonging to the same symmetry class then lead to the energies and forms of the molecular orbitals given in the Appendix and to the energy-level scheme shown in Figure 3. These calculations also show that in this compound the central metal ion configuration is $V(\ldots 3d^{4.016}\,4s^{0.524}\,4p^{0.104})$ and that its charge is $+0{\cdot}356|e|$ where e is the electronic

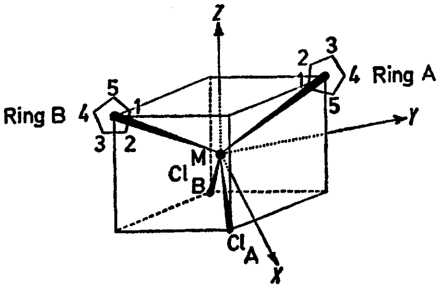

FIGURE 2

charge. Provided spin–orbit coupling, Zeeman and hyperfine interactions are all ignored, then the unpaired electron lies in the antibonding $A_1{}^*$ orbital indicated in Figure 3. This has the general form

$$\begin{aligned}\psi^*(A_1) = {} & \alpha_1{}^*[ad_{x^2-y^2} + bd_{z^2} + cs + dp_z] + \\ & \alpha_1{}^{*(\mathrm{I})}p_x[A_1] + \alpha_1{}^{*(\mathrm{II})}p_z[A_1] + \alpha_1{}^{*(\mathrm{III})}\mathrm{cp}_0[A_1] + \\ & \alpha_1{}^{*(\mathrm{IV})}\mathrm{cp}_1[A_1] + \alpha_1{}^{*(\mathrm{V})}\mathrm{cp}_2[A_1]\end{aligned}$$

but in fact our molecular orbital calculations show that in this particular case only contributions from the metal ion $d_{x^2-y^2}$ and d_{z^2} orbitals and from the chloride ion p_x orbitals are important and so $\psi^*(A_1)$ simplifies to the form given in (3). The general forms of the bonding and antibonding orbitals of B_1 and B_2 symmetry which lie within ± 2 e.v. from the $\psi^*(A_1)$ orbital are also given in (3) in order of increasing energy. In these, the

$$\begin{aligned}\psi(B_2) &= \beta_2 d_{yz} + \beta_2{}^{(\mathrm{I})}\mathrm{cp}_0[B_2] + \beta_2{}^{(\mathrm{II})}\mathrm{cp}_1[B_2] + \\ &\qquad \beta_2{}^{(\mathrm{III})}\mathrm{cp}_2[B_2] + \beta_2{}^{(\mathrm{IV})}p_y[B_2] \\ \psi(B_1) &= \beta_1 d_{xz} + \beta_1{}^{(\mathrm{I})}\mathrm{cp}_1[B_1] + \beta_1{}^{(\mathrm{II})}\mathrm{cp}_2[B_1] + \\ &\qquad \beta_1{}^{(\mathrm{III})}p_z[B_1] + \beta_1{}^{(\mathrm{IV})}p_x[B_1] \\ \psi^*(A_1) &= \alpha_1{}^*(ad_{x^2-y^2} + bd_{z^2}) + \alpha_1{}^{*(\mathrm{I})}p_x[A_1] \\ \psi^*(B_2) &= \beta_2{}^*d_{yz} + \beta_2{}^{*(\mathrm{I})}\mathrm{cp}_0[B_2] + \beta_2{}^{*(\mathrm{II})}\mathrm{cp}_1[B_2] + \\ &\qquad \beta_2{}^{*(\mathrm{III})}\mathrm{cp}_2[B_2] + \beta_2{}^{*(\mathrm{IV})}p_y[B_2] \\ \psi^*(B_1) &= \beta_1{}^*d_{xz} + \beta_1{}^{*(\mathrm{I})}\mathrm{cp}_1[B_1] + \beta_1{}^{*(\mathrm{II})}\mathrm{cp}_2[B_1] + \\ &\qquad \beta_1{}^{*(\mathrm{III})}p_z[B_1] + \beta_1{}^{*(\mathrm{IV})}p_x[B_1]\end{aligned} \tag{3}$$

metal ion $4p_x$ orbital has been omitted from linear combinations of B_1 symmetry and the metal ion $4p_y$ orbital from combinations with B_2 symmetry; their contributions are small and they do not influence the magnetic properties of this complex.

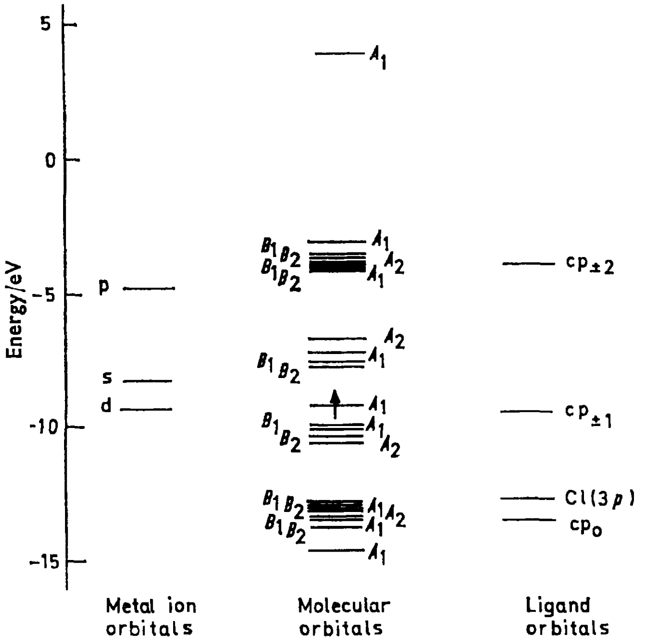

FIGURE 3 Molecular orbital energy-level diagram for $(\pi\text{-}C_5H_5)_2VCl_2$

Spin–orbit coupling at the central metal ion and at the chloride ions, Zeeman interactions and hyperfine interactions all perturb the combinations of the orbital functions (3) with the various allowed electronic spin functions, and if the matrix elements of the second and third of these interactions are equated [25] with those of the spin-Hamiltonian (1) then the spin-Hamiltonian parameters can be expressed as functions of the coefficients of the molecular orbitals. If the approximations

$$P_{md}(B_2{}^*) + P_{md}(B_2) \approx 1 \text{ and } P_{md}(B_1{}^*) + P_{md}(B_1) \approx 1$$

where $P_{md}(\psi)$ is the metal ion d-orbital population in the orbital ψ, are made, and if the influence of ligand spin–orbit coupling on the magnetic properties of these complexes are neglected, then these functions may be shown to be:

$$\begin{aligned}g_{xx} = {} & 2{\cdot}002 - \{2(\alpha_1{}^*)^2(a + b\sqrt{3})^2\xi_{\mathrm{v}}\} \\ & \left\{\frac{P_{md}(B_2{}^*)}{\Delta E[\psi^*(B_2) \leftarrow \psi^*(A_1)]} - \frac{[1 - P_{md}(B_2{}^*)]}{\Delta E[\psi^*(A_1) \leftarrow \psi(B_2)]}\right\}\end{aligned} \tag{5}$$

$$\begin{aligned}g_{yy} = {} & 2{\cdot}002 - \{2(\alpha_1{}^*)^2(a - b\sqrt{3})^2\xi_{\mathrm{v}}\} \\ & \left\{\frac{P_{md}(B_1{}^*)}{\Delta E[\psi^*(B_1) \leftarrow \psi^*(A_1)]} - \frac{[1 - P_{md}(B_1{}^*)]}{\Delta E[\psi^*(A_1) \leftarrow \psi(B_1)]}\right\}\end{aligned} \tag{6}$$

$$g_{zz} \approx 2{\cdot}002 \tag{7}$$

$$\begin{aligned}T_{xx} = P\Big\{ & -\kappa + \frac{2}{7}(a^2 - b^2)(\alpha_1{}^*)^2 - \\ & 4\frac{\sqrt{3}}{7}ab(\alpha_1{}^*)^2 + (g_{xx} - 2{\cdot}002) + \\ & \frac{1}{14}\frac{(3a + b\sqrt{3})}{(a - b\sqrt{3})}(2{\cdot}002 - g_{yy}) - \frac{1}{7}\frac{b}{a}(2{\cdot}002 - g_{zz})\Big\}\end{aligned} \tag{8}$$

$$\begin{aligned}T_{yy} = P\Big\{ & -\kappa + \frac{2}{7}(a^2 - b^2)(\alpha_1{}^*)^2 + \\ & 4\frac{\sqrt{3}}{7}ab(\alpha_1{}^*)^2 + (g_{yy} - 2{\cdot}002) + \\ & \frac{1}{14}\frac{(3a - b\sqrt{3})}{(a + b\sqrt{3})}(2{\cdot}002 - g_{xx}) + \frac{1}{7}\frac{b}{a}(2{\cdot}002 - g_{zz})\Big\}\end{aligned} \tag{9}$$

$$\begin{aligned}T_{zz} = P\Big\{ & -\kappa - \frac{4}{7}(a^2 - b^2)(\alpha_1{}^*)^2 - \\ & \frac{1}{14}\frac{(3a + b\sqrt{3})}{(a - b\sqrt{3})}(2{\cdot}002 - g_{yy}) - \\ & \frac{1}{14}\frac{(3a - b\sqrt{3})}{(a + b\sqrt{3})}(2{\cdot}002 - g_{xx}) + (g_{zz} - 2{\cdot}002)\Big\}\end{aligned} \tag{10}$$

Small contributions of the order of $-0{\cdot}002$, which are due to spin–orbit mixing of orbitals of A_2 symmetry have been omitted from (7). $P = 2{\cdot}002 g_N \beta_e \beta_N \langle d_{z^2}{}^* | r^{-3} | d_{z^2} \rangle$ and is shown in the Appendix to be $0{\cdot}01065$ cm^{-1} for $(\pi\text{-}C_5H_5)_2VCl_2$. ξ_{v} is the spin–orbit coupling constant for the vanadium ion in the valence state appropriate to $(\pi\text{-}C_5H_5)_2VCl_2$, *i.e.* to vanadium in a $V^{+0{\cdot}356}(\ldots 3d^{4{\cdot}016}\ 4s^{0{\cdot}524}\ 4p^{0{\cdot}104})$ state, and by the method outlined in the Appendix its value can be shown to be $+133$ cm^{-1}. The corresponding values in the niobium complex $(\pi\text{-}C_5H_5)_2NbCl_2$ are estimated to be $P = 0{\cdot}01086$ cm^{-1}

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[25] B. R. McGarvey, 'Transition Metal Ion Chemistry,' Edward Arnold, London, 1966, **3**, 89.

and $\xi_{Nb} = +490$ cm^{-1} respectively. Adding equations (5)—(7) and dividing each side by **3** gives

$$a \approx -P\kappa - [2{\cdot}002 - \langle g \rangle]P \qquad (11)$$

where $\langle g \rangle = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$ and $a = \frac{1}{3}(T_{xx} + T_{yy} + T_{zz})$.

Bonding in the Metallocene Derivatives $(\pi\text{-}C_5H_5)_2VX_2$ and $(\pi\text{-}C_5H_5)_2NbX_2$.—Values of κ and of the parameters a, b, and $\alpha_1{}^*$ involved in the $\psi^*(A_1)$ molecular orbital can be estimated from equations (8)—(11) and are listed in Table **3**. The relative signs of the coefficients a and b cannot be determined directly from the paramagnetic resonance data, nor is it possible to determine from this data which of the experimentally estimated g-tensor components should be assigned to g_{xx} and which to g_{yy}. However, Hückel calculations indicate that a and b have opposite signs so that g_{xx} must be the larger component and the smaller value must be assigned to g_{yy}. The metal ion d-orbital populations in the $\psi^*(B_2)$ and $\psi^*(B_1)$ orbitals, $P_{md}(B_2{}^*)$ and $P_{md}(B_1{}^*)$ may then be estimated from equations (5) and (6).

TABLE 3

Molecular orbital coefficients and metal ion d-orbital populations for the metallocene complexes $(\pi\text{-}C_5H_5)_2VX_2$ and $(\pi\text{-}C_5H_5)_2NbX_2$. Bracketed data are obtained if the last terms in equations (5) and (6) are omitted in estimating metal ion d-orbital populations

Complex	κ	$\lvert a \rvert$	$\lvert b \rvert$	$(\alpha_1{}^*)^2$	$P_{md}(B_2{}^*)$	$P_{md}(B_1{}^*)$
$(\pi\text{-}C_5H_5)_2VCl_2$	0·64	0·223	0·975	0·97	0·553 (0·348)	0·582 (0·392)
$(\pi\text{-}C_5H_5)_2V(SCN)_2$	0·64	0·247	0·969	0·917	0·586 (0·370)	0·776 (0·658)
$(\pi\text{-}C_5H_5)_2V(OCN)_2$	0·66	0·237	0·971	0·946	0·605 (0·425)	0·762 (0·643)
$(\pi\text{-}C_5H_5)_2V(CN)_2$	0·53	0·238	0·971	0·83	0·577 (0·296)	0·595 (0·333)
$(\pi\text{-}C_5H_5)_2NbCl_2$	0·98	0·274	0·963	1·00	0·456 (0·166)	0·520 (0·350)
$(\pi\text{-}C_5H_5)_2Nb(SCN)_2$	0·94	0·294	0·956	0·942	0·475 (0·149)	0·585 (0·324)
$(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2$	0·85	0·276	0·962	0·915	0·455	0·440
$(\pi\text{-}C_5H_5)_2Nb(CN)_2$	0·77	0·325	0·946	0·808	0·438 (0·072)	0·504 (0·167)

The magnitude of $(\alpha_1{}^*)^2$ is a measure of the degree of delocalisation of the unpaired electron away from the central metal ion on to the two σ-bonded ligands. The data in Table **3** show that in both the vanadium and niobium series of compounds, with the exception of the cyanides, there is little delocalisation of this electron; $\psi^*(A_1)$ essentially is a non-bonding metal ion orbital. Furthermore, the character of the metal ion contribution to $\psi^*(A_1)$ hardly changes if the σ-bonded ligands are changed; in both the vanadium and niobium series it consists of a metal ion d_{z^2} orbital mixed with a small amount of the corresponding metal ion $d_{x^2-y^2}$ orbital.

The magnitude of $[1 - P_{md}(B_2{}^*)]$ is, in practice, a measure of the extent of delocalisation of the π-cyclopentadienide residue into metal ion d_{yz} orbitals. The data in Table **3** and in Figure **3** are all consistent in showing that these electrons are completely delocalised and are shared almost equally between the aromatic rings and the central metal ions. The magnetic resonance data also show that there is more delocalisation in the niobium series than in the corresponding vanadium compounds. It is worth noting in this context that if the charge-transfer contributions represented by the last term in equation (5) are omitted when equating g_{xx} to the molecular orbital parameters, then gross underestimates of the values of $P_{md}(B_2{}^*)$ and hence gross overestimates of the extent of delocalisation of these electrons result; the bracketed data in Table **3** are estimates obtained when these charge-transfer contributions are not taken into account. $[1 - P_{md}(B_1{}^*)]$ provides a similar measure of the extent of delocalisation of σ electrons away from the ligands X into the central metal ion d_{xz} orbitals. Table **3** again shows that considerable delocalisation of these electrons also occurs and that there is more delocalisation in the niobium series than in the vanadium series; it also shows that the π-cyclopentadienide residues are more strongly bonded to the central metal ions than the σ-bonded ligands.

APPENDIX

A. *Molecular Orbital Analysis of* $(\pi\text{-}C_5H_5)_2VCl_2$.—The molecular geometry was assumed to have the distorted tetrahedral form shown in Figure **2**. Use was made of structural data for which *X*-ray or electron diffraction analyses are available[26-29] assuming the normals through the centres of the cyclopentadienide rings pass through the vanadium ion, the angles $(\pi\text{-}C_5H_5)\text{-}V\text{-}(\pi\text{-}C_5H_5)$ and Cl–V–Cl to be 125 and 95° respectively, the V–C distances to be 2·25 Å, and the V–Cl distances to be 2·10 Å.

Single-exponent Slater-type atomic orbitals of the kind described by Cusachs *et al.*[30,31] were then used to estimate overlap integrals S_{ij} between basis orbitals i and j. Coulomb integrals, H_{ii}, were set equal to the valence state ionisation potentials of the appropriate basis atomic orbitals, ionisation potentials for Cl$^-$ and $(\pi\text{-}C_5H_5)^-$ orbitals being derived from data given in ref. 32, and ionisation potentials for central metal-ion basis orbitals, corrected to take charge and configuration

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[26] W. N. Lipscomb and A. G. Whittaker, *J. Amer. Chem. Soc.*, 1945, **67**, 2019.

[27] G. Engebretson and R. E. Rundle, *J. Amer. Chem. Soc.*, 1963, **85**, 481.

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[29] M. A. Bush and G. A. Sim, *J. Chem. Soc.* (*A*), 1971, 2225.

[30] L. C. Cusachs, B. L. Trus, D. G. Carroll, and S. P. McGlynn, *Internat. J. Quantum Chem.*, 1967, **1**, 423.

[31] L. C. Cusachs and J. H. Corrington, 'Sigma Molecular Orbital Theory,' O. Sinanoglu and K. W. Wiberg, Yale University Press, Newhaven, 1970, 256.

[32] V. I. Vedeneyev, L. V. Gurvich, N. N. Kondrat'yev, M. A. Medvedev, and Ye. L. Frankevich, 'Bond Energies, Ionisation Potentials, and Electron Affinities,' Edward Arnold, London, 1966.

effects into account, being obtained by the methods described in ref. 33. Resonance integrals, H_{ij}, were evaluated from these overlap and Coulomb integrals using the Wolfsberg–Helmholz approximation[34] and

$$H_{ij} = 0{\cdot}85\, S_{ij}(H_{ii} + H_{jj})$$

the secular equations were then diagonalised using standard techniques.[33,35] The computed atom charges and orbital populations were then used to estimate new H_{ii} values and the cycle of calculations then repeated until the input and output charge associated with each atom coincided.

TABLE 4

Energy levels and atomic orbital coefficients in the LCAO molecular orbital description of $(\pi\text{-}C_5H_5)_2VCl_2$. Molecular orbitals are in symmetry classes appropriate to the C_{2v} group. Energies are in units of eV. The unpaired electron is in the starred A_1 orbital

A_1 Symmetry

	Atomic orbital coefficients								
Energy	4*s*	$4p_z$	d_{z^2}	$d_{x^2-y^2}$	$p_z[A_1]$	$p_x[A_1]$	$cp_0[A_1]$	$cp_1[A_1]$	$cp_2[A_1]$
−14·50	−0·305	+0·004	+0·041	+0·073	−0·088	+0·147	+0·757	+0·004	−0·000
−13·33	−0·090	−0·023	−0·190	−0·223	−0·847	+0·097	−0·167	−0·037	+0·000
−12·93	+0·042	−0·034	−0·123	+0·064	−0·133	−0·931	+0·237	−0·004	−0·000
−10·03	+0·025	+0·013	+0·247	+0·299	−0·287	−0·016	−0·104	+0·832	+0·000
−9·21 *	−0·010	−0·036	+0·755	−0·645	−0·027	−0·199	+0·069	+0·009	−0·012
−7·24	+0·063	−0·339	+0·543	+0·656	−0·336	+0·054	−0·132	−0·475	+0·007
−3·89	+0·002	−0·009	−0·027	+0·039	−0·001	+0·008	−0·002	−0·001	−1·000
−2·99	+0·173	+0·982	+0·267	+0·247	−0·380	−0·132	+0·018	−0·405	−0·007
+4·09	+1·262	−0·161	−0·093	−0·123	−0·279	+0·416	+0·953	+0·08	+0·002

A_2 Symmetry

	Atomic orbital coefficients			
Energy	d_{xy}	$p_z[A_2]$	$cp_1[A_2]$	$cp_2[A_2]$
−12·99	−0·224	−0·939	+0·053	−0·002
−10·64	+0·538	−0·284	−0·687	−0·003
−6·67	+0·865	−0·239	+0·774	−0·082
−3·84	+0·135	−0·032	+0·079	+0·998

B_1 Symmetry

	Atomic orbital coefficients					
Energy	$4p_x$	d_{xz}	$p_y[B_1]$	$p_x[B_1]$	$cp_1[B_1]$	$cp_2[B_1]$
−13·23	−0·002	−0·299	+0·548	−0·697	+0·031	+0·007
−12·82	+0·051	−0·001	+0·778	+0·610	+0·003	+0·000
−9·91	−0·064	−0·368	−0·146	+0·220	−0·852	−0·009
−7·53	−0·153	+0·895	+0·304	−0·317	+0·470	+0·101
−3·79	+0·479	−0·121	−0·115	−0·045	+0·107	+0·891
−3·47	+0·912	+0·230	−0·109	−0·222	+0·335	−0·456

B_2 Symmetry

	Atomic orbital coefficients					
Energy	$4p_y$	d_{yz}	$p_y[B_2]$	$cp_0[B_2]$	$cp_1[B_2]$	$cp_2[B_2]$
−13·63	−0·020	+0·179	−0·149	−0·945	+0·018	−0·002
−12·94	+0·039	−0·154	+0·938	−0·227	−0·024	+0·002
−10·17	+0·024	+0·500	+0·203	+0·163	+0·768	+0·005
−7·67	+0·212	+0·837	+0·173	+0·177	−0·635	+0·044
−3·91	+0·432	−0·012	−0·112	−0·046	+0·063	−0·907
−3·64	+0·911	−0·257	−0·284	−0·141	+0·218	+0·423

The final estimated electronic configuration at the vanadium ion turned out to be $V(\ldots 3d^{4{\cdot}016}\ 4s^{0{\cdot}524}\ 4p^{0{\cdot}104})$ and the final charge distribution, in units of electronic charge, was:

Atom or group	V	$\pi\text{-}C_5H_5$	Cl
Charge	+0·356	+0·457	−0·635

The final eigenvalues and eigenfunctions are listed in Table 4 and the resultant energy level diagram is shown in Figure 3. If electron–electron repulsions are ignored then this molecular orbital calculation predicts the one-electron transition energies in the visible region of the spectrum to be:

Transition	Type	Energy (cm^{-1})
1	$B_2^* \leftarrow A_1^*$	12 100
2	$B_1^* \leftarrow A_1^*$	13 500
3	$(A_1^*)' \leftarrow A_1^*$	16 100
4	$A_2^* \leftarrow A_1^*$	20 100

A comparison of these predictions with the experimental data in Table 1 forces us to assign the stronger absorption observed at 11 800 cm^{-1} in the spectrum of $(\pi\text{-}C_5H_5)_2VCl_2$ to transitions 1 and 2, and the weaker band observed at 13 600 cm^{-1} to transition 3. Transition 4 is forbidden in C_{2v} symmetry. No peak has been detected in the 20 000 cm^{-1} region of the $(\pi\text{-}C_5H_5)_2VCl_2$ spectrum, but a weak absorption is easily detected in this region in the spectrum of $(\pi\text{-}C_5H_5)_2NbCl_2$, in addition to a stronger absorption at 17 000 cm^{-1}.

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[33] C. J. Ballhausen and H. B. Gray, 'Molecular Orbital Theory,' W. A. Benjamin, Inc., New York, 1965, 120.

[34] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

[35] D. A. Brown in 'Transition Metal Ion Chemistry,' R. L. Carlin, ed., Edward Arnold, London, 1963, **3**, 1.

The Hückel calculation implies that the π-cyclopentadienide rings are more strongly bound to the central metal ion. It gives values for $P_{md}(B_2^*)$ and $P_{md}(B_1^*)$ of 0·57 and 0·66 respectively, in good agreement with the deductions made from the magnetic resonance measurements, and it also supports these deductions in that the unpaired electron lies essentially in a non-bonding metal ion orbital. However, it appears to overestimate the magnitude of the $3d_{x^2-y^2}$ contribution to this orbital.

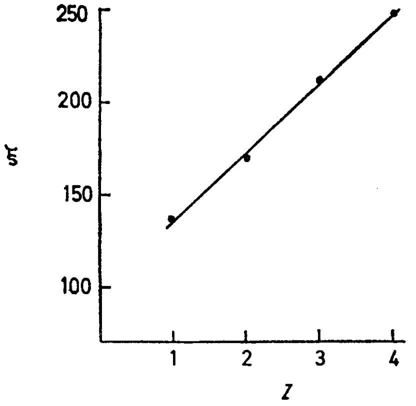

FIGURE 4 Spin–orbit coupling constants ξ(cm^{-1}), for vanadium ions *vs.* ionic charge, *Z*

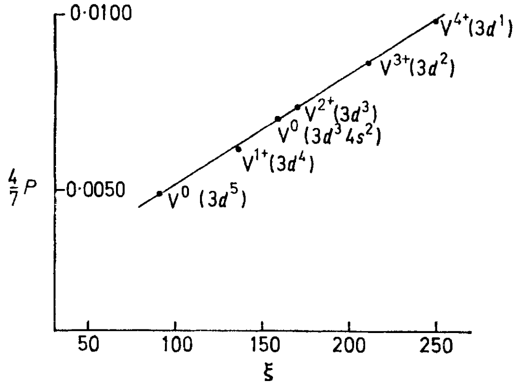

FIGURE 5 Spin–orbit coupling constants ξ(cm^{-1}), for various vanadium ion configurations *vs.* $\frac{4}{7}P$ cm^{-1}

(B). ξ and *P* Values.—Figure 4 is obtained when the free-ion values of the spin–orbit coupling constants, ξ, for vanadium ions are plotted against the charges on the ions;[36] it shows that for a vanadium ion with a charge of +0·356 electronic units and a configuration $3d^{4\cdot644}$, ξ = 115 cm^{-1}. For vanadium(0) in a $3d^5$ configuration ξ = 91 cm^{-1};[37] for vanadium(0) in a $3d^34s^2$ configuration ξ = 158 cm^{-1}.[36,37] Promoting an electron from a 3*d* to a 4*s* orbital therefore increases ξ by 33 cm^{-1} and hence, promoting 0·6 of an electron from $V^{+0\cdot356}(3d^{4\cdot644})$ to $V^{+0\cdot356}(3d^{4\cdot016}\ 4s^{0\cdot524}\ 4p^{0\cdot104})$ increases ξ to 133 cm^{-1}. Figure 5 is obtained[37] when $\frac{4}{7}$ *P* is plotted against ξ; it predicts a value of $P = 0\cdot01065$ cm^{-1} for vanadium(IV) in $(\pi\text{-}C_5H_5)_2VCl_2$. In the niobium series, *P* was obtained by applying equations (8)—(11) to the experimental hyperfine coupling tensors and ξ then estimated from the data[37] on Figure 6 for niobium(IV) in $(\pi\text{-}C_5H_5)_2NbCl_2$; this procedure gives $P = 0\cdot01086$ cm^{-1} and ξ = +490 cm^{-1}.

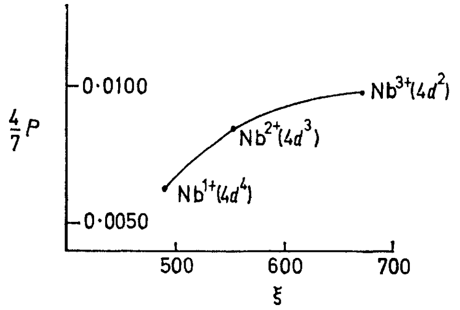

FIGURE 6 Spin–orbit coupling constants ξ(cm^{-1}), for various niobium ion configurations *vs.* $\frac{4}{7}P$ cm^{-1}

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[2/2239 *Received, 25th September,* 1972]

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