Niobium Organometallic Chemistry. Part 6.† Electron Spin Resonance Study of Bonding in Pseudo-tetrahedral Bis(η-cyclopentadienyl)niobium(IV) Complexes

By **Clement Sanchez, Daniel Vivien,** and **Jacques Livage,*** Spectrochimie du solide, Laboratoire associé au C.N.R.S. LA 302, E.N.S.C.P., 11, rue Pierre et Marie Curie, 75231 Paris, France
Jean Sala-Pala, Bernard Viard, and **Jacques-E. Guerchais,*** Equipe de recherche associée au C.N.R.S. ERA 822, Université de Bretagne Occidentale, 29283 Brest-Cedex, France

X-Band e.s.r. spectra of two $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}]^+$ complexes (R = C_2H_5 or i-C_3H_7) have been recorded at room temperature and 77 K. They show interaction of the unpaired electron with the ^{93}Nb and the ^{31}P nuclei. A detailed analysis of spin-Hamiltonian parameters is given and the bonding is discussed assuming that the ligand field around niobium has C_{2v} symmetry. The strong and almost isotropic superhyperfine coupling of the unpaired electron with the ^{31}P nucleus is interpretable in terms of delocalization through the sulphur atoms.

WE recently reported that bis(η^5-cyclopentadienyl)niobium dichloride $[NbCl_2(\eta\text{-}C_5H_5)_2]$ reacts with sulphur-containing ligands affording niobium cationic species such as $[Nb(\eta\text{-}C_5H_5)_2(S_2CNR_2)]^+$ and $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}]^+$.[1,2] Such pseudo-tetrahedral niobium(IV) complexes are paramagnetic and may be studied by e.s.r. spectroscopy. Owing to the presence of a phosphorus atom, superhyperfine coupling arises in the *OO'*-dialkyl dithiophosphate complexes and these are more suitable than the dithiocarbamates for the investigation of the electronic properties.

We report here the results of our studies on the e.s.r. and optical spectra of the $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}][PF_6]$ complexes. The data are discussed in terms of the energy levels and bonding parameters, assuming a distorted (C_{2v}) tetrahedral ligand field around niobium.

EXPERIMENTAL

The $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}][PF_6]$ complexes (R = C_2H_5 or i-C_3H_7) were prepared by treating dichlorobis(η-cyclopentadienyl)niobium with tetraphosphorus decasulphide in the appropriate alcohol.[2]

Electron spin resonance spectra of acetone solutions of $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}][PF_6]$ (R = C_2H_5 or i-C_3H_7) were recorded on an *X*-band JEOL ME 3X spectrometer. Experiments at 77 K were performed using an insertion quartz Dewar. The magnetic field was measured with a n.m.r. proton probe and the microwave frequency with a wave meter giving an accuracy of ±1 MHz. A computer program was developed to simulate the e.s.r. spectra of d^1 ions ($S = \frac{1}{2}$) with orthorhombic *g* and *A* tensors (assuming coincident axes of both tensors) and a superhyperfine tensor with one $I = \frac{1}{2}$ nucleus. The line shape was taken as a Gaussian or Lorentzian first derivative. The angular dependence of the resonant field and the transition intensities, taking into account second-order terms, were taken from Sakaguchi *et al.*[3] The frozen-solution spectra were calculated by accumulating the spectra corresponding to different orientations of the magnetic field towards the *g* and *A* tensor axes. These orientations were obtained by subdividing the triangular faces of a regular icosahedron into several triangles giving 93, 345, and 1 329 orientations per octant.[4]

RESULTS

Figure 1(*a*) shows the room-temperature e.s.r. spectrum recorded on an acetone solution of $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}][PF_6]$. It exhibits the superposition of two ten-line spectra due to the hyperfine coupling of the 4*d* unpaired electron ($S = \frac{1}{2}$) of a Nb^{4+} ion with the nuclear spin ($I = \frac{9}{2}$) of the 100% abundant ^{93}Nb isotope. Each of these

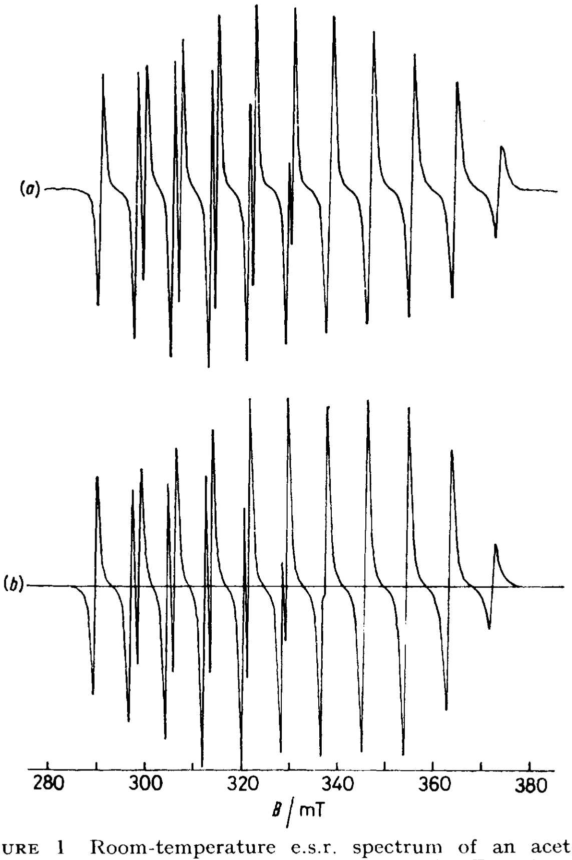

FIGURE 1 Room-temperature e.s.r. spectrum of an acetone solution of $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}][PF_6]$. (*a*) Experimental spectrum, (*b*) simulated spectrum

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† Part 5, I. Bkouche-Waksman, C. Bois, J. Sala-Pala, and J. E. Guerchais, *J. Organometallic Chem.*, 1980, **195**, 307.

lines is split into two, showing strong superhyperfine coupling with the ^{31}P nucleus ($i = \frac{1}{2}$) of the dithiophosphate ligand. The two sets of hyperfine lines actually overlap on the high-field side of the spectrum and due to the line width (*ca.* 20 G) * they cannot be separated as shown by the computer simulation presented in Figure 1(*b*). The spectrum can be described using the isotropic spin Hamiltonian (1) where A and I refer to the Nb nucleus while a and i

$$\mathscr{H}_{\text{iso.}} = g_{\text{iso.}}\beta\hat{\boldsymbol{H}}\cdot\hat{\boldsymbol{S}} + A_{\text{iso.}}\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{S}} + a_{\text{iso.}}\hat{\boldsymbol{i}}\cdot\hat{\boldsymbol{S}} \qquad (1)$$

refer to the phosphorus. The measured values are listed in Table 1.

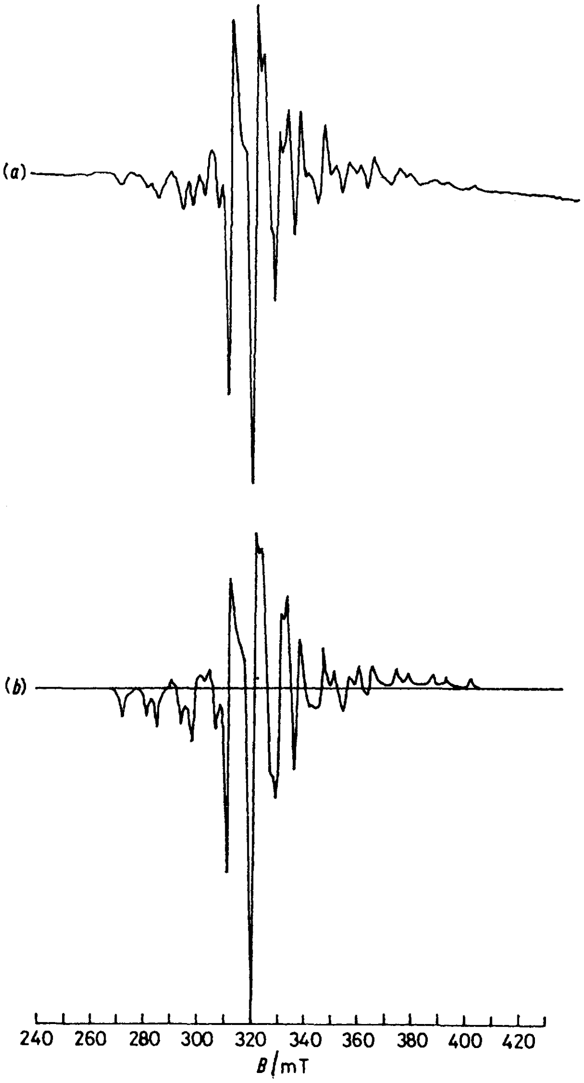

FIGURE 2 Frozen-solution e.s.r. spectrum of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\{\text{S}_2\text{P}(\text{OR})_2\}][\text{PF}_6]$ recorded at 77 K. (*a*) Experimental spectrum, (*b*) simulated spectrum

The frozen-solution spectrum (Figure 2) also exhibits hyperfine and superhyperfine features due to the coupling of the unpaired electron with the ^{93}Nb and ^{31}P nuclei. A straightforward analysis of this spectrum can be made assuming that the ligand field around Nb^{4+} has a C_{2v} symmetry. Since the quadrupolar interactions at the central ion appear to be very small, and assuming that g and A tensor axes are coincident, the spin Hamiltonian can be written in the diagonal form (2).

$$\hat{\boldsymbol{H}} = g_{xx}\beta\hat{\boldsymbol{H}}_x\,.\,\hat{\mathbf{S}}_x + g_{yy}\beta\hat{\boldsymbol{H}}_y\hat{\mathbf{S}}_y + g_{zz}\beta\hat{\boldsymbol{H}}_z\hat{\mathbf{S}}_z + A_{xx}\hat{\mathbf{S}}_x\hat{\boldsymbol{I}}_x + A_{yy}\hat{\mathbf{S}}_y\hat{\boldsymbol{I}}_y + A_{zz}\hat{\mathbf{S}}_z\hat{\boldsymbol{I}}_z + a_{xx}\hat{\mathbf{S}}_x\hat{\boldsymbol{i}}_x + a_{yy}\hat{\mathbf{S}}_y\hat{\boldsymbol{i}}_y + a_{zz}\hat{\mathbf{S}}_z\hat{\boldsymbol{i}}_z \qquad (2)$$

All spin-Hamiltonian parameters were determined from computer simulation. The best fit was obtained using a Lorentzian derivative line shape and an isotropic line width. The results are listed in Table 1. There is no significant change in any of the parameters for the two dithiophosphates studied; this suggests that the nature of the alkyl groups of the sulphur-containing ligand has little influence on the electronic properties of the complex.

TABLE 1

Spin Hamiltonian parameters of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\{\text{S}_2\text{P}(\text{OR})_2\}]$-$[\text{PF}_6]$ acetone solutions. All hyperfine tensor components are in 10^{-4} cm^{-1}

		R = ethyl	R = isopropyl
g tensor	g_{xx}	1.999	1.999
	g_{yy}	2.001	2.000
	g_{zz}	1.963	1.962
	$g_{\text{iso.}}$	1.988	1.988
^{93}Nb hyperfine tensor	A_{xx}	−47.6	−46.7
	A_{yy}	−79.4	−78.4
	A_{zz}	−123.2	−123.7
	$A_{\text{iso.}}$	−75.7	−75.6
^{31}P superhyperfine tensor	a_{xx}	85.2	86.5
	a_{yy}	85.2	86.5
	a_{zz}	85.0	85.2
	$a_{\text{iso.}}$	85.1	86.0

DISCUSSION

Molecular Orbitals.—Our results were analyzed by assuming a C_{2v} ligand-field symmetry around Nb^{4+} (x, y, and z axes are chosen as in Figure 3). Our e.s.r. spectra indicate that, in agreement with previous studies [5-8] on tetrahedrally co-ordinated vanadium(IV) and niobium(IV) complexes, the ground state is $^2A_1$. Molecular-orbital calculations and e.s.r. experiments by Stewart

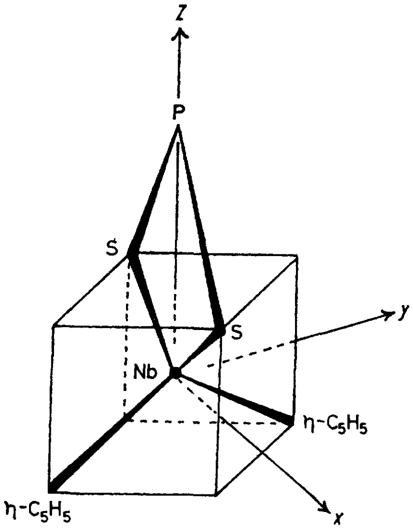

FIGURE 3 Ligand-field symmetry of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\{\text{S}_2\text{P}(\text{OR})_2\}]^+$

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* Throughout this paper: 1 G = 10^{-4} T.

and Porte on similar complexes[5,6] indicate that the main contribution of the metal ion to the ground state comes from $d_{x^2-y^2}$ and d_{z^2} orbitals. The 5s and 5p_z contributions can, to a first approximation, be neglected. The a_1 molecular orbitals will then be described by the linear combination of three wave functions: the metal $4d_{x^2-y^2}$ and d_{z^2} orbitals, and one ligand orbital combination, L_{A_1}, having 'A_1' symmetry. We then have three molecular orbitals corresponding to the general expression (3) where $a^2 + b^2 = 1$.

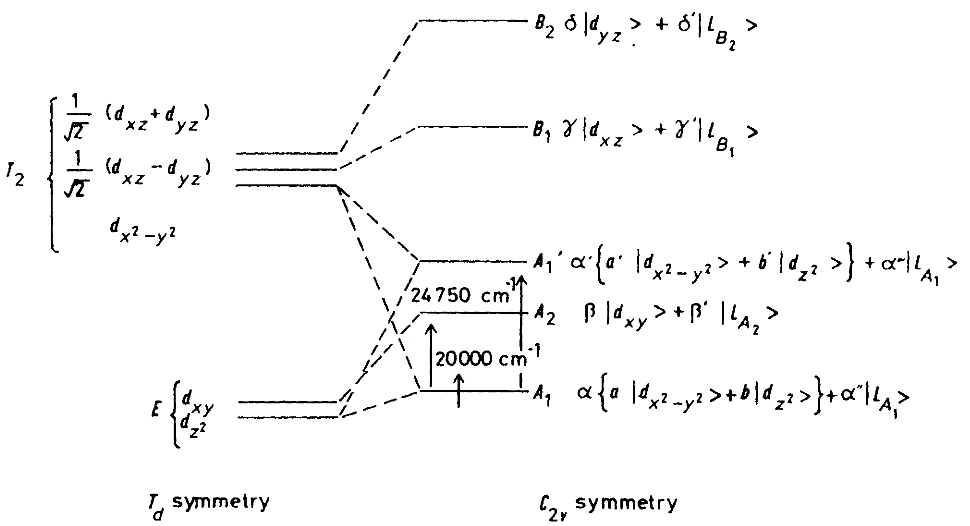

FIGURE 4 d energy-level splitting in $[\mathrm{Nb}(\eta\text{-}\mathrm{C_5H_5})_2\{\mathrm{S_2P(OR)_2}\}][\mathrm{PF_6}]$. In the molecular-orbital expression $|L\Gamma_i\rangle$ represents the ligand-orbital combination having Γ_i symmetry

$$\psi_{A_1} = \alpha(a|d_{x^2-y^2}\rangle + b|d_{z^2}\rangle) + \alpha''|L_{A_1}\rangle \quad (3)$$

The lowest energy ψ_{A_1} bonding orbital will be mainly of ligand character while the highest antibonding orbital will be mainly of metal character. The middle one, roughly non-bonding, could exhibit both ligand and metal character.

The C_{2v} component of the ligand field mixes the niobium $4d_{x^2-y^2}$ and $4d_{z^2}$ atomic orbitals, so the question arises which orbital lies lower? As already mentioned by Stewart and Porte,[5] e.s.r. parameters can be used quickly to distinguish whether the unpaired electron in a tetrahedral complex lies in a $d_{x^2-y^2}$ or a d_{z^2} orbital. If it were in d_{z^2}, we would have g_{xx} and g_{yy} smaller than $g_{zz} \simeq g_e$[9] as in $[\mathrm{NbX_2}(\eta\text{-}\mathrm{C_5H_5})_2]$ (X = Cl, SCN, or OCN) complexes.[5] Our e.s.r. experiments show that g_{zz} is smaller than g_{xx} and g_{yy}. This indicated that the unpaired d electron lies in a $d_{x^2-y^2}$ orbital. Mixing of $4d_{z^2}$ character into this orbital accounts for the 'in-plane anisotropy' of the g tensor. The C_{2v} component of the ligand field being relatively weak, we may assume that $a \gg b$ in the ground state. The excited states corresponding to the antibonding molecular orbitals are shown in Figure 4.

Electron Spin Resonance Parameters and Molecular-orbital Coefficients.—Spin–orbit coupling, the Zeeman effect, and hyperfine coupling will perturb the basic wave functions. Identifying the matrix elements of these interactions with those of the spin Hamiltonian leads to expressions for the e.s.r. parameters as functions of the molecular-orbital coefficients. For an unpaired $d_{x^2-y^2}$ electron in a C_{2v} ligand field, these functions are given in equations (4)—(9).[10-13] In these expressions, the small b^2 terms have been neglected, λ is the spin–orbit coupling constant of the Nb ion in the

$$g_{xx} = g_e - \frac{2a(a + 2\sqrt{3}b)\ \alpha^2\gamma^2\lambda}{E_{xz} - E_{x^2-y^2}} \quad (4)$$

$$g_{yy} = g_e - \frac{2a(a - 2\sqrt{3}b)\ \alpha^2\delta^2\lambda}{E_{yz} - E_{x^2-y^2}} \quad (5)$$

$$g_{zz} = g_e - \frac{8a^2\alpha^2\beta^2\lambda}{E_{xy} - E_{x^2-y^2}}, \quad (6)$$

$$A_{xx} = P[-K + \frac{2}{7}a^2\alpha^2 - \frac{4\sqrt{3}}{7}ab - (g_e - g_{xx}) + \frac{1}{14}\frac{(3a + \sqrt{3}b)}{(a - \sqrt{3}b)}(g_e - g_{yy}) - \frac{1}{7}\frac{b}{a}(g_e - g_{zz})] \quad (7)$$

$$A_{yy} = P[-K + \frac{2}{7}a^2\alpha^2 + \frac{4\sqrt{3}}{7}ab - (g_e - g_{yy}) + \frac{1}{14}\frac{(3a - \sqrt{3}b)}{(a + \sqrt{3}b)}(g_e - g_{xx}) + \frac{1}{7}\frac{b}{a}(g_e - g_{zz})] \quad (8)$$

$$A_{zz} = P[-K - \frac{4}{7}a^2\alpha^2 - \frac{1}{14}\frac{(3a + \sqrt{3}b)}{(a - \sqrt{3}b)}(g_e - g_{yy}) - \frac{1}{14}\frac{(3a - \sqrt{3}b)}{(a + \sqrt{3}b)}(g_e - g_{xx}) - (g_e - g_{zz})] \quad (9)$$

valence state appropriate to the complex, K is the isotropic Fermi contact term, and $P = g_e\beta_e g_n\beta_n \langle d_{x^2-y^2}|r^{-3}|d_{x^2-y^2}\rangle$. From these equations we can deduce equations (10)—(12). We have assumed here that all A parameters are negative as already reported in the literature for niobium(IV) complexes.[5,14]

The measured e.s.r. parameters (Table 1), together with equations (4) to (12), allow us to calculate a^2, b^2, α^2, and K. It is not possible with the paramagnetic resonance data alone to determine either the relative signs of a and b, or which of the in-plane g tensor components should be attributed to g_{xx} or g_{yy}. According to our x and y assignment as indicated in Table 1, it follows that a and b should have opposite signs. Interchange of x and y axes would lead to the same sign for a and b. Calculations of a, b, α, and K were made with the P and λ values corresponding to the Nb^+ formal oxidation state. This takes into account the screening effect of the negatively charged ligands and corresponds to the $P = 0.010\,86$ cm^{-1} value found by Stewart and Porte[5] in $[NbCl_2(\eta\text{-}C_5H_5)_2]$. Calculations made with P and λ values corresponding to a higher oxidation state (Nb^{2+}, Nb^{3+}, or Nb^{4+}) would give much lower α values ($\alpha^2 \simeq 0.3$) than we could reasonably expect, indicating a much stronger delocalization of the unpaired electron.

$$\langle A\rangle = -P(K + g_e - \langle g\rangle) \qquad (10)$$

$$\langle A\rangle = \tfrac{1}{3}\,(A_{xx} + A_{yy} + A_{zz}) \qquad (11)$$

$$\langle g\rangle = \tfrac{1}{3}(g_{xx} + g_{yy} + g_{zz}) \qquad (12)$$

Results are collected in Table 2. They are quite similar to those previously found for another tetrahedral niobium(IV) complex $[Nb(NR_2)_4]$ where the unpaired electron also lies in a $d_{x^2-y^2}$ orbital.[14] On the other hand, K and α appear to be somewhat smaller than in tetrahedral $[NbX_2(\eta\text{-}C_5H_5)_2]$ (X = Cl, SCN, OCN, or CN) where the ground state is mainly of d_{z^2} character[5] (a, 0.27—0.32; b, 0.946—0.963). This indicates a stronger delocalization of the unpaired $4d_{x^2-y^2}$ electron towards the ligands.

TABLE 2

Molecular-orbital coefficients calculated from e.s.r. parameters

	K	$\lvert a\rvert$	$\lvert b\rvert$	α^2
R = ethyl	0.74	0.989	0.148	0.60
R = isopropyl	0.74	0.989	0.149	0.61

Ultraviolet–Visible Absorption Spectra.—A typical u.v.–visible absorption spectrum of a solution of $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}][PF_6]$ in acetone is shown in Figure 5. Intense charge-transfer bands can be seen around 28 000 cm^{-1}. They can be assigned to transitions in which an electron is transferred from a cyclopentadienyl ring molecular orbital to that orbital which contains the unpaired electron.[5] Broad and weak absorption bands appear between 20 000 and 25 000 cm^{-1}. They presumably correspond to $d\leftarrow d$ transitions. A straightforward calculation shows that whatever may be the exact value of γ^2 and δ^2, the corresponding $B_1\leftarrow A_1$ and $B_2\leftarrow A_1$ transitions lie quite far into the u.v. region where they should be hidden by more intense charge-transfer transitions. The two broad bands observed at 24 750 and 20 000 cm^{-1} should then be attributed to the $A_1'\leftarrow A_1$ and $A_2\leftarrow A_1$ transitions. The last should actually be forbidden because none of the x, y, or z components of the electrical dipole moment μ_e has A_2 symmetry in the C_{2v} group. We then have $\langle A_1|\mu_e|A_2\rangle = 0$. This is not the case for the integral $\langle A_1|\mu_e|A_1'\rangle$ and the corresponding transition should have a higher intensity. We could then assume the following assignments: $A_2\leftarrow A_1$ at 20 000 cm^{-1} and $A_1'\leftarrow A_1$ at 24 750 cm^{-1}.

Neglecting overlap effects, an approximate value of β^2 can then be deduced from ref. 5 giving $\beta^2 = 0.33$. This indicates a strong participation of the ligand orbitals in the A_1 ground state ($\alpha^2 = 0.66$) as well as in the A_2 excited state ($\beta^2 = 0.33$).

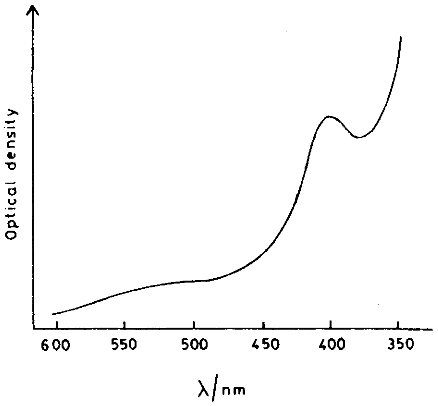

FIGURE 5 U.v.–visible absorption spectrum of an acetone solution of $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}][PF_6]$

From these results, we could suggest a correlation diagram giving the atomic orbital energy levels of the Nb^{4+} ion in the complex (Figure 4).

Superhyperfine Coupling with ^{31}P.—A strong superhyperfine coupling of the $4d$ unpaired electron with the ^{31}P nucleus is observed (Table 1). It appears even stronger than the hyperfine coupling with the Nb nucleus. Such high values have already been reported for ^{31}P or ^{75}As superhyperfine interactions in similar complexes.[8,15-17] In our case, they are somewhat larger than those previously found for a vanadium dithiophosphinate complex.[15] This can be correlated to the larger extension of the $4d$ orbitals, giving a greater overlap with the ligand orbitals.

Table 1 shows that the superhyperfine tensor is almost isotropic. This suggests that the phosphorus orbitals involved in the interaction must be mostly 's' in character. A direct overlap of the $4d_{z^2}$ metal orbital with the $3s$ phosphorus orbital could account for such a high hyperfine coupling. But, as the $4d_{z^2}$ contribution in the ground-state wave function appears to be quite small (Table 2), we do not believe that this is the main mechanism. We thus suggest an indirect interaction through a σ overlap between the Nb $4d_{x^2-y^2}$ orbital and an appropriate linear combination at the two P–S σ-bonding orbitals.[15,18] The strong delocalization of the unpaired $4d_{x^2-y^2}$ electron indicated by the low α^2 value (Table 2) could account for such a high superhyperfine interaction.

The isotropic ^{31}P coupling may be estimated from equation (13) where α_P is the coefficient of the phosphorus 3*s* atomic orbital involved in the molecular orbital containing the unpaired electron.

$$a_P = \frac{8}{3}\pi g_e g_n \beta_e \beta_n |\psi_{3s}(0)|^2 \alpha_P^2 \qquad (13)$$

For ^{31}P we have equation (14),[9,10] we then get $\alpha_P^2 = 0.025$ and $\alpha_P = 0.158$.

$$\frac{8}{3}\pi g_e g_n \beta_e \beta_n |\psi_{3s}(0)|^2 = 3.231 \times 10^{-4}\ \text{cm}^{-1} \qquad (14)$$

Conclusion.—Like their vanadium analogues, the e.s.r. spectra of the $[Nb(\eta\text{-}C_5H_5)_2\{S_2P(OR)_2\}]^+$ cations exhibit an hyperfine and a superhyperfine coupling of the unpaired electron with the metallic and phosphorus nuclei. The superhyperfine coupling with the ^{31}P nucleus is quite strong (*ca.* 90 G) and even stronger than the hyperfine coupling with the ^{93}Nb nucleus (*ca.* 75 G). It is almost isotropic and is interpretable in terms of delocalization through the sulphur atoms. While in the $[NbX_2(\eta\text{-}C_5H_5)_2]$ complexes (X = Cl, SCN, or OCN) the unpaired electron was shown to be essentially in a d_{z^2} orbital, the e.s.r. data for the dithiophosphates are indicative of a mainly $d_{x^2-y^2}$ ground state.

[0/347 *Received*, 3*rd March*, 1980]

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