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Niobium Organometallic Chemistry. Part III.* Reaction of Bis(cyclopentadienyl)niobium Dichloride with Tetraphosphorus Decasulphide. E.S.R. and N.M.R. Studies of some Niobium(IV) and Niobium(V) O,O′-dialkyldithiophosphates

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The reaction of $(\eta^5\text{-}C_5H_5)_2NbCl_2$ *with* P_4S_{10} *in an alcohol ROH affords two types of compounds:*

(i) paramagnetic niobium(IV) complexes formulated as $[(\eta^5\text{-}C_5H_5)_2Nb[S_2P(OR)_2]]^+PF_6^-$. *The e.s.r. spectra correspond to the interaction of the unpaired electron with the* ^{93}Nb *and* ^{31}P *nuclei. They show a significant delocalization over the phosphorus and indicate the unpaired electron lies in the* $d_{x^2-y^2}$ *orbital;*

(ii) diamagnetic niobium(V) complexes $[(\eta^5\text{-}C_5H_5)_2NbS_2[SP(S)(OR)_2]]$ *containing an* NbS_2 *ring, for which* ^1H, ^{13}C *and* ^{31}P *n.m.r. data are given.*

Introduction

In recent years, niobium(IV) chemistry has been widely explored. Most of the reported complexes are paramagnetic compounds having *cis* or *trans* pseudo-octahedral configuration [1–3] [$[NbX_4L_2]$ with X = Cl, Br and L = pyridine, phosphine ...; $[NbCl_6]^{2-}$; ...] or a dodecahedral structure [$[NbX_4(AA)_2]$ with X = Cl, Br, I and AA = *o*-phenylenebisdimethylarsine [4] or $[Nb(BB)_4]$ with BB = dialkyldithiocarbamate [5–7], ...]. Some pseudo-tetrahedral niobium(IV) complexes have also been described [$[NbX_4]$ with X = dialkylamine [8]] but they are rather uncommon in coordination chemistry and it was therefore of interest to investigate the $[(\eta^5\text{-}C_5H_5)_2NbX_2]$ organometallic derivatives. Some compounds of this type are well known (X = Cl, $\sigma\text{-}C_5H_5$, CH_3 ... [9–11]) and their e.s.r. spectra have been reported [11–13]. Curiously, no complexes with X ligands containing atoms with a nucleus spin I have been studied up to now, excepted the cases with X = H, Cl and CH_3 [11, 12, 14]. We thought it of interest to synthesize such complexes with phosphorus-containing ligands and to study them by e.s.r., this technique being, in such cases, one of the most valuable tools to obtain detailed information about the electron distribution and the nature of the metal–ligand interaction.

We therefore undertook a study of the reaction of the bis(cyclopentadienyl)niobium dichloride $[(\eta^5\text{-}C_5H_5)_2NbCl_2]$ [9] with P_4S_{10} in various alcohols, anticipating that we would find some striking differences with the previously reported results obtained with vanadium [15], the first transition element in this group. That such differences would be found was suggested by the existence of well-characterized bis(cyclopentadienyl) derivatives of niobium(V) [16–18] whereas the vanadium analogues do not exist.

Therein, we report the synthesis and e.s.r. study of several niobium(IV) O,O′-dialkyldithiophosphates of the formula $[(\eta^5\text{-}C_5H_5)_2Nb[S_2P(OR)_2]]^+PF_6^-$. The preparation and n.m.r. study of several niobium(V) O,O′-dialkyldithiophosphates are also reported.

Experimental

General Procedures

All reactions were performed in Schlenk tubes in a dry oxygen-free nitrogen atmosphere. Elemental analyses were performed by the Service Central de Microanalyses du C.N.R.S.

Physical Measurements

Infrared spectra were recorded on a PYE-UNICAM spectrophotometer from 200 to 4000 cm^{-1} (nujol mulls between caesium iodide windows). ^1H, ^{13}C and ^{31}P n.m.r. spectra were obtained on a JEOL FX 100 using d-3 chloroform as a solvent.

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*Part II: J. Sala-Pala, J. Amaudrut, J. E. Guerchais, R. Mercier and M. Cerutti, *J. Fluor. Chem.*, *14*, 269 (1979).

ESR spectra of acetone solutions were recorded at 10^4 MHz on a JEOL ME3X apparatus with a TE_{011} mode cylindrical cavity. Low temperature spectra of frozen solutions were recorded at 130 K by blowing cold nitrogen gas through the cavity. The magnetic field was measured with a proton n.m.r. probe and the microwave frequency with a wavemeter giving an accuracy of ±1 MHz.

The conductance measurements were performed at 22 °C with a TACUSSEL CD 7N conductivity bridge on approximately $10^{-3}M$ solutions (solvent: nitromethane, dried over molecular sieves and deoxygenated before use).

Materials

The complex $(\eta^5\text{-}C_5H_5)_2NbCl_2$ was prepared as described by LUCAS [9]. P_4S_{10} and NH_4PF_6 were purchased from PROLABO and MERCK and used without further purification. All solvents were distilled by standard techniques and thoroughly deoxygenated before use.

Preparation and Study of the Bis(η^5-cyclopentadienyl)O,O'-dialkyldithiophosphatoniobium(IV) hexafluorophosphates $[(\eta^5\text{-}C_5H_5)_2Nb[S_2P(OR)_2]]^+PF_6^-$ (Complexes I)

To a solution of P_4S_{10} (300 mg) in the appropriate alcohol (*ca.* 60 cm^3), $[(\eta^5\text{-}C_5H_5)_2NbCl_2]$ in excess (2 g) was added. The mixture was stirred (5–6 hours; *ca.* 40 °C) and the resulting solution was filtered. To the brown filtrate (A) was immediately added an excess of NH_4PF_6 dissolved in the same alcohol. A brown microcrystalline powder quickly precipitated. This was filtered, washed with chloroform and water and dried under vacuum.

When R = Et, i-Pr, this powder was the pure required product. When R = Me, the pure product may be obtained from a recrystallisation in hot methanol. Yield *ca.* 20%.

When R = t-Bu, only impure material was obtained even after chromatography and the only reported data for this complex are the e.s.r. data (see Table I).

R = Me

Analysis: Calcd.: C, 27.4; H, 3.0; S, 12.9; Found: C, 27.7; H, 3.2; S, 11.8.

*i.r.**: (200–1200 cm^{-1}) 290 m, 348 w, 388 w, 430 w, 521 m and 558 s (ν_{4PF_6} and ν_{PS}), 645 vs (ν_{PS}), 740 m, 800–840 vs (ν_{3PF_6} and γ_{CH}), 1020 vs, 1050 sh, 1175 w.

R = Et

Analysis: Calcd.: C, 30.4; H, 3.6; S, 11.6; P, 11.2. Found: C, 30.3; H, 3.9; S, 11.4; P, 10.9.

i.r.: 300 w, 357 vw, 404 vw, 539 m and 562 s (ν_{4PF_6} and ν_{PS}), 646 s (ν_{PS}), 748 sh, 785 s, 800 sh, 830 s br (γ_{CH} and ν_{3PF_6}), 850 sh, 886 s, 1025 s br, 1101 vw, 1160 w.

R = i-Pr

Analysis: Calcd.: C, 33.0; H, 4.1; S, 11.0; P, 10.7. Found: C, 32.3; H, 4.2; S, 10.8; P, 10.1.

i.r.: 290 m, 317 w, 351 vw, 370 vw, 382 vw, 396 vw, 436 sh, 455 m, 541 s and 552 s (ν_{4PF_6} and ν_{PS}), 630 s (ν_{PS}), 730 w, 761 w, 820–840 vs br (ν_{3PF_6} and γ_{CH}), 878 s, 970 vs br, 1019 sh, 1100 m, 1140 m, 1175 m.

Conductivities: The found values for the molar conductances Λ (Ω^{-1} cm^2 mol^{-1}: 111 for R = Me; 95 for R = Et; 108 for R = i-Pr) for *ca.* $10^{-3}M$ solutions in nitromethane are within the range expected for 1:1 electrolytes [19].

E.S.R.: E.S.R. data for these compound are given in Table I. Typical spectra in acetone solution at room temperature and at 130 K are shown in Fig. 1 and 2.

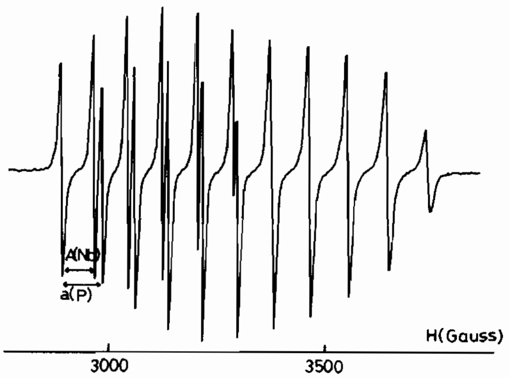

Fig. 1. E.S.R.: acetone solution spectrum of $[Cp_2NbS_2P(OEt)_2]^+$ recorded at room temperature.

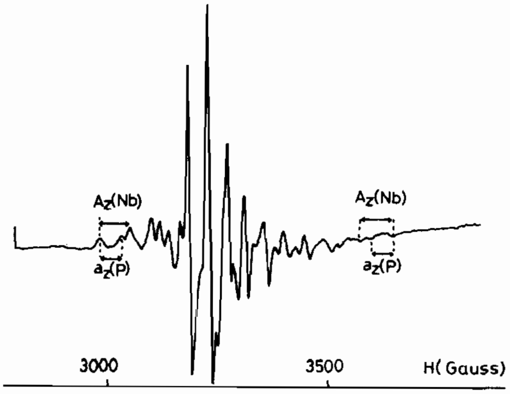

Fig. 2. E.S.R.: frozen solution spectrum of $[Cp_2NbS_2P(OEt)_2]^+$ recorded at 130 K.

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*I.R. abbreviations: vs: very strong; s: strong; m: medium; w: weak; vw: very weak; br: broad; sh: shoulder.

TABLE I. E.S.R. Parameters.

R	g	g_z	$\frac{1}{2}(g_x + g_y)$	Hyperfine Coupling with ^{93}Nb (Gauss)			Superhyperfine Coupling with ^{31}P (Gauss)		
				A	A_z	$\frac{1}{2}(A_x + A_y)$	a	a_z	$\frac{1}{2}(a_x + a_y)$
Me	1.989	1.983	1.991	81.5	138.5	53.0	96.8	91.0	99.7
Et	1.988	1.963	2.000	81.6	134.4	55.2	91.7	92.7	91.2
i-Pr	1.988	1.963	2.001	81.5	135.0	54.8	92.7	93.0	92.6
t-Bu	1.991	1.974	1.999	83.9	133.8	59.0	93.2	94.6	92.6

Physical properties: All these compounds are brown to dark-brown in colour and slightly sensitive to moisture and oxygen. They are stable in an inert and dry atmosphere. They possess disagreable odour and are soluble in acetone but only very sparingly soluble in water and in chloroform.

Preparation and Study of the Bis(η^5-cyclopentadienyl)disulfuroO,O′-dialkyldithiophosphatoniobium(V) Complexes (η^5-$C_5H_5)_2NbS_2[SP(S)(OR)_2]$ (Complexes II)

To the solution (A) described above was added a solution of P_4S_{10} (300 mg) in the same alcohol (*ca.* 60 cm^3). After concentration (volume reduced to *ca.* 60 cm^3) orange crystals precipitated after one or two days. They were filtered, washed with water and dried under vacuum. This treatment afforded the required complex for R = Et and i-Pr.

For R = Me, the pure compound was obtained by extraction of the above precipitate with chloroform and then recrystallisation in methanol.

When R = t-Bu, the pure product was prepared as follows: the above crystals were dissolved in THF and chromatographed on an alumina column made up in benzene. Elution with CH_2Cl_2 or THF gave an orange band from which the required product was obtained by concentration. Yields *ca.* 20% for R = Et, i-Pr; *ca.* 10% for R = Me, t-Bu.

The title complexes may also be synthesized using sulphur. To the solution (A), sulphur in excess was added. The mixture was stirred (for *ca.* 12 hours) at *ca.* 40 °C. An orange powder precipitated. It was filtered and extracted with the appropriate hot alcohol. The required compound precipitated from the extract.

R = Me

Analysis: Calcd.: C, 32.4; H, 3.6; S, 28.8. Found: C, 32.5; H, 4.3; S, 29.6.

i.r.: 227 w, 282 m, 301 w, 319 m, 375 w, 400 w, 424 w, 533 m and 552 m (ν_{SS} and ν_{PS}), 620 s (ν_{PS}), 770 s, 785 s, 832 s (γ_{CH}), 865 m, 947 sh, 1008 s, 1030 s br, 1073 w, 1170 m.

*^1H n.m.r.**: 3.84, d, (CH_3), $^3J_{P-H}$ = 14; 6.05, s, (C_5H_5).

^{13}C n.m.r.: 53.6, d, (CH_3), $^2J_{P-C}$ = 9; 109.0, s, (C_5H_5).

R = Et

Analysis: Calcd.: C, 35.6; H, 4.2; S, 27.1; P, 6.6. Found: C, 35.4; H, 4.1; S, 26.9; P, 6.3.

i.r.: 265 vw, 305 w, 337 vw, 375 vw, 400 vw, 543 vs and 550 sh (ν_{SS} and ν_{PS}), 667 vs (ν_{PS}), 757 sh, 778 s, 792 sh, 824 m and 835 m (γ_{CH}), 867 m, 886 vw, 950 vs, 1015 s, 1044 s, 1080 sh, 1104 vw, 1155 m.

^1H n.m.r.: 1.42, t, (CH_3), $^3J_{H-H}$ = 7.0; 4.38, m, (CH_2), $^3J_{H-H}$ = 7.0, $^3J_{P-H}$ = 9.0; 6.10, s, (C_5H_5).

^{13}C n.m.r.: 16.1, d, (CH_3), $^3J_{P-C}$ = 9; 63.2, d, (CH_2), $^2J_{P-C}$ = 9; 109.0, s, (C_5H_5).

^{31}P n.m.r.: 111.3, qu, $^3J_{P-H}$ = 9.0.

R = i-Pr

Analysis: Calcd.: C, 38.4; H, 4.8; S, 25.6. Found: C, 38.1; H, 4.9; S, 24.3.

i.r. : 268 vw, 291 w, 376 w, 400 vw, 439 w, 458 w, 521 s and 550 m (ν_{PS} and ν_{SS}), 663 vs (ν_{PS}), 731 w, 772 w, 828 s (γ_{CH}), 870 m, 880 sh, 889 w, 955 vs, 990 vs, 1010 sh, 1030 sh, 1070 w, 1105 s, 1128 sh, 1141 w, 1179 m.

^1H n.m.r.: 1.42, d of d, (CH_3), $^3J_{H-H}$ = 6.2, $^4J_{P-H}$ = 2.6; 4.95, m, (CH), $^3J_{H-H}$ = 6.2; $^3J_{P-H}$ = 12.1; 6.08, s, (C_5H_5). (see Fig. 3).

^{13}C n.m.r.: 24.1, d, (CH_3), $^3J_{P-C}$ = 6; 72.2, d, (CH), $^2J_{P-C}$ = 8; 109.0, s, (C_5H_5).

^{31}P n.m.r.: 108.9, t, $^3J_{P-H}$ = 12.1.

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*^{1}H and ^{13}C n.m.r. data given as: δ (ppm/TMS), nature of the signal, (assignment), coupling constant (Hz).
s = singlet; d = doublet; t = triplet; qu = quintuplet; m = multiplet.
^{31}P n.m.r. data given as = δ (ppm/H_3PO_4), nature of the signal, coupling constant (Hz).

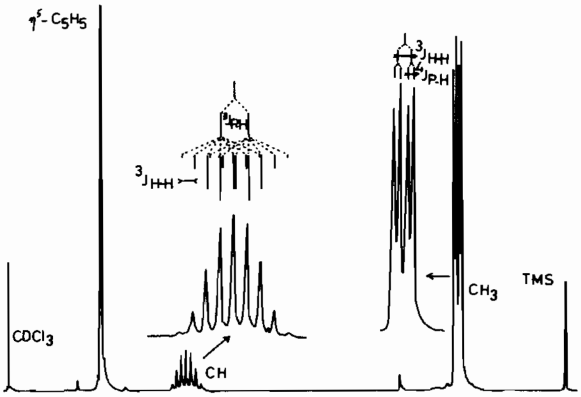


Fig. 3. ^1H n.m.r.: d3 chloroform solution spectrum of $[Cp_2NbS_2[SP(S)(OPr)_2]]$ recorded at room temperature.

R = t-Bu

Analysis: Calcd.: C, 40.9; H, 4.8; S, 24.2; Nb, 17.6; P, 5.9. Found: C, 40.9; H, 5.5; S, 24.2; Nb, 16.8; P, 6.7.

i.r.: 280 w, 310 w, 360 w, 375 w, 460 sh, 470 m, 531 s and 550 m (ν_{PS} and ν_{SS}), 620 vs (ν_{PS}), 670 s, 700 vs, 725 m, 736 m, 820 vs (γ_{CH}), 830 m, 880 w, 910 vs, 950 vs, 980 vs, 1010 m, 1025 w, 1040 m, 1070 w, 1165 vs, 1250 s.

^1H n.m.r.: 1.70, s, (CH_3); 6.10, s, (C_5H_5).

^{13}C n.m.r.: 30.6, d, (CH_3), $^3J_{P-C}$ = 3; 85.2, d, (CMe_3), $^2J_{P-C}$ = 11; 108.8, s, (C_5H_5).

Conductivities: The found values for *ca.* $10^{-3}M$ solutions in nitromethane (Λ in Ω^{-1} cm^2 mol^{-1}: 4.6 for R = Me; 0.5 for R = Et; 2.6 for R = i-Pr; 4.3 for R = t-Bu) correspond to the presence of undissociated molecular complexes.

Physical properties: These orange compounds are not air-sensitive. They are soluble in chloroform but insoluble in acetone and water.

Remark about the Mass Spectra

Mass spectra were scanned only for complexes (I) and (II) with R = Et.

The highest peak on the mass spectrum of complex (I), noted at m/e 408, corresponds to the expected cation ($C_{14}H_{20}NbO_2PS_2^+$ = 408). For complex (II), surprisingly no peak appears at the expected value for the parent peak $C_{14}H_{20}NbO_2PS_4^+$ = 474) while a peak is observed at m/e 408 (M – S_2).

Results

When added to an alcoholic solution of P_4S_{10}, $[(\eta^5\text{-}C_5H_5)_2NbCl_2]^9$ dissolves, giving a red-brown solution from which two kinds of products may be isolated. Addition of ammonium hexafluorophosphate in excess gives complexes (I) while addition of an alcoholic solution of P_4S_{10} leads to compounds (II).

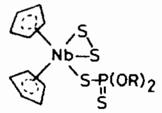
The elemental analyses of complexes (I) are in agreement with $[(\eta^5\text{-}C_5H_5)_2Nb[S_2P(OR)_2]^+PF_6^-$, the formulation of (I) as niobium(IV) derivatives being clearly supported by e.s.r. (*vide infra*).

Analytical results for complexes (II) indicate a $[PS_2(OR)_2]^-$/Nb ratio equal to 1 like for compounds (I) but they also show the surprising presence of two supplementary sulphur atoms per niobium. The diamagnetism of the compounds, obvious from the sharpness of the n.m.r. peaks, indicates that niobium probably exists in its +V formal oxidation state.

Infrared Data

Infrared data and tentative assignments for complexes (I) and (II) are presented in the experimental part. They provide very little useful structural information other than establishing the presence of η^5-cyclopentadienyl and O,O′-dialkyldithiophosphate groups. The lack of published informations about the i.r. frequencies of the $[S_2P(OR)_2]$ group precludes attempts to distinguish between monodentate or bidentate coordination of this ligand. Bands arising from the $[S_2P(OR)_2]$ group occur consistently in the following regions: 1065–905 cm^{-1} (ν_{CO}); 875–730 cm^{-1} (ν_{PO}); 650–550 cm^{-1} (ν_{PS}) and 1240–1085 cm^{-1} (deformations involving the carbon atoms) [20]. PF_6^- anions in compounds (I) are characterized by a strong and broad absorption assignable to $\nu_{3(F_{1u})}$ at 800–850 cm^{-1} (superposed with a strong absorption γ_{CH} of the cyclopentadienyl groups) and a sharp peak near 550 cm^{-1} assignable to $\nu_{4(F_{1u})}$ [21].

We previously reported the preparation of disulphurniobium(V) complexes by oxidation of niobium (IV) derivatives with elemental sulphur [22]. The existence of the NbS_2 three-membered ring was deduced from the presence, on the i.r. spectra, of a strong and sharp band at 540 cm^{-1} assignable to ν_{SS}. The presence of such a ring in compounds (II) is not very obvious from i.r. data since superposition of the presumed ν_{S-S} peak with a ν_{P-S} band of the dialkyldithiophosphate group occurs. However, the well-established existence of NbS_2 rings and the 18 electron rule lead us to suggest the following structure for complexes (II):



This structure seems more likely than those with a bidentate dithiophosphate ligand and two cyclopentadienyl groups respectively acting as a five and a three electron ligand like in $(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)W(CO)_2$ [23].

N.M.R. Data

The n.m.r. resonances of the diamagnetic compounds (II) are readily assigned and are consistent with the above formulation of these complexes (see experimental part and Fig. 3). Splittings arising from spin–spin coupling with ^{31}P (I = 1/2) are observed. The values for the chemical shifts and the spin–spin coupling are in good agreement with those found in the literature. Despite our efforts, no ^{93}Nb and ^{33}S n.m.r. spectra could be recorded.

E.S.R. Data

Figure 1 shows the ESR spectrum of an acetone solution of $[Cp_2Nb[S_2P(OEt)_2]]^+PF_6^-$ recorded at room temperature. It exhibits the superposition of two ten-line spectra. These ten lines result from the hyperfine coupling of a 4d unpaired electron with the ^{93}Nb nucleus ($I_{Nb} = \frac{9}{2}$) indicating the presence of paramagnetic Nb^{4+} species. Each of these lines is split into two components. This splitting can be attributed to a superhyperfine coupling of the 4d unpaired electron with the ^{31}P nucleus ($I_P = \frac{1}{2}$) of the dithiophosphate group. Such a solution spectrum can be described with an isotropic spin hamiltonian:

$$\underset{\sim}{\mathcal{H}} = g\beta HS + ASI + aSi$$

where A and I are respectively the hyperfine coupling parameter and the nuclear spin of the Nb nucleus, while a and i are those of the P nucleus.

The frozen solution spectra (Fig. 2) recorded at 130 K also exhibit the hyperfine and superhyperfine features due to the coupling of an unpaired 4d electron with the ^{93}Nb and ^{31}P nuclei. They can be described* using an orthorhombic spin Hamiltonian:

$$\begin{aligned}\underset{\sim}{\mathcal{H}} = {} & g_z\beta H_zS_z + g_x\beta H_xS_x + g_y\beta H_yS_y \\ & + A_zS_zI_z + A_xS_xI_x + A_yS_yI_y \\ & + a_zS_zi_z + a_xS_xi_x + a_yS_yi_y\end{aligned}$$

where A and I refer to the Nb nucleus while a and i refer to the P nucleus (the z axis is chosen along the Nb–P direction).

The isotropic and 'z' components can be easily measured on the experimental spectra. The 'x' and 'y' components can only be estimated using the relations:

$$g_x + g_y = 3g - g_z$$
$$A_x + A_y = 3A - A_z$$
$$a_x + a_y = 3a - a_z$$

These parameters are gathered in Table I.

The site symmetry around Nb^{4+} is C_{2v}, the C_2 axis lying along the Nb–P direction. In such a tetrahedral complex, the unpaired electron could be described either by a $d_{x^2-y^2}$ or d_{z^2} orbital. According to the theory of the g tensor, the g values would be:

in a d_{z^2} orbital: $g_z = g_e; g_x = g_e - \dfrac{6\lambda}{E_{xz} - E_{z^2}}$;

$$g_y = g_e - \frac{6\lambda}{E_{yz} - E_{z^2}}$$

in a $d_{x^2-y^2}$ orbital: $g_z = g_e - \dfrac{8\lambda}{E_{xy} - E_{x^2-y^2}}$;

$$g_x = g_e - \frac{2\lambda}{E_{xz} - E_{x^2-y^2}};$$

$$g_y = g_e - \frac{2\lambda}{E_{yz} - E_{x^2-y^2}} \quad \text{where } g_e = 2.0023.$$

The measured g values show that, in our case, g_z is different from g_e and smaller than g_x and g_y. The unpaired electron must then be in the $d_{x^2-y^2}$ orbital.

The isotropic hyperfine coupling parameters are larger with ^{31}P than with ^{93}Nb indicating a strong delocalization of the unpaired electron toward the phosphorus orbitals. Such a delocalization appears to be more important in our case with niobium complexes than with similar vanadium complexes [12, 15, 24]. It is also worth nothing that the hyperfine coupling with phosphorus appears to be almost isotropic which suggests that the P orbitals involved in the interaction must be mostly s in character.

Discussion

The dissolution of P_4S_{10} in an alcohol ROH leads to the formation of the corresponding O,O'-dialkyldithiophosphoric acid $HSP(S)(OR)_2$ according to reaction (1) [25]:

$$P_4S_{10} + 8ROH \longrightarrow 4HSP(S)(OR)_2 + 2H_2S \qquad (1)$$

The synthesis of complexes (I), similar to the vanadium derivatives already described by Casey *et al.* [15], can be easily explained by a reaction like:

$$[(\eta^5\text{-}C_5H_5)_2NbCl_2] + HSP(S)(OR)_2 + NH_4PF_6 \longrightarrow [(\eta^5\text{-}C_5H_5)_2Nb[SP(S)(OR)_2]]^+PF_6^- + HCl + NH_4Cl \qquad (2)$$

The surprising formation of diamagnetic niobium (V) compounds from $[(\eta^5\text{-}C_5H_5)_2NbCl_2]$ clearly shows the ease of oxidation of niobium(IV) in such complexes. This is a striking difference with vanadium since up to date and as expected all

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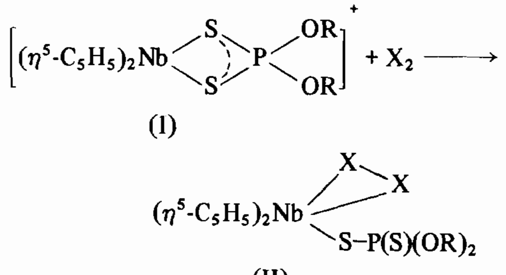
*A more detailed analysis using computer simulation is going on at the moment and will be published in a forthcoming paper.

attempts to obtain similar diamagnetic vanadium(V) complexes from $(\eta^5\text{-}C_5H_5)_2VCl_2$, P_4S_{10} and an alcohol were unsucessful.

Some doubts remain about the synthesis of the diamagnetic niobium derivatives and particularly concerning the origin of the two sulphur atoms of the NbS_2 ring, which according to reaction (1) may arise from the dialkyldithiophosphoric acid in excess or from hydrogen disulphide. Although H_2S can react to give niobium(V) complexes with the NbS_2 moiety [for example, $(\eta^5\text{-}C_5H_5)_2NbS_2Cl$ is prepared by bubbling H_2S through an alcoholic solution containing $(\eta^5\text{-}C_5H_5)_2NbCl_2(OH)$ and KCl [26]], we do not think that such a way is possible here, the niobium being only in its +IV oxidation state in the starting material and hydrogen disulphide having well-known reducing properties. The two extra sulphur atoms may arise from by products of the alcoholysis of P_4S_{10} which, according to Moedritzer *et al.* [27], affords not only H_2S and the dithiophosphoric acid $HSP(S)(OR)_2$ but also one to four other sulphur derivatives in low yield.

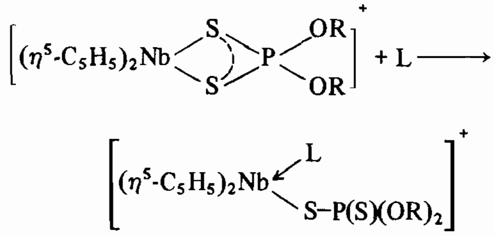
In $[VO(S_2PR_2)_2]$ complexes, the two dialkyldithiophosphinate groups act as bidentate ligands but the e.s.r. study shows that when pyridine is added, coordination of pyridine occurs in solution, one of the two $[S_2PR_2]$ groups acting then as a monodentate ligand [24]. If we rule out niobium oxidation, formation of complexes (II) from complexes (I) can be also regarded as a transformation of the three-electron dithiophosphate ligand into a one-electron ligand by action of a two-electron ligand of the X_2 type (S_2^{2-}) according to reaction (3):


(I)

(II)

(3)

Up to now all attempts to isolate, in the solid state, compounds corresponding to similar transformations using a two-electron ligand of the L type like phosphines and phosphine sulphides (according to reaction 4) were unsuccessful:


(4)

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