

## PREPARATION AND SPECTRAL STUDIES OF DITHIOPHOSPHATE AND DITHIOPHOSPHINATE COMPLEXES OF DICYCLOPENTADIENYLVANADIUM(IV)

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### Summary

The dithiophosphate and dithiophosphinate complexes  $[\text{Cp}_2\text{V} \begin{matrix} \text{S} \\ \diagdown \\ \diagup \\ \text{S} \end{matrix} \text{PR}_2]^+ [\text{S}_2\text{PR}_2]^-$  ( $\text{R} = \text{Et}, \text{OEt}, \text{OPr}^i$ ) can be conveniently prepared by reaction of  $\text{Cp}_2\text{V}$  with the disulphides  $[\text{SP}(\text{S})\text{R}_2]_2$  in THF; all products have been characterized by IR and EPR spectroscopy and conductivity measurements. The EPR spectra of the complexes have been recorded in solution at room temperature and in glasses; they show isotropic interaction of the unpaired electron with the  $^{51}\text{V}$  and  $^{31}\text{P}$  nuclei, which can be accounted for in terms of delocalization through the sulphur atoms.

### Introduction

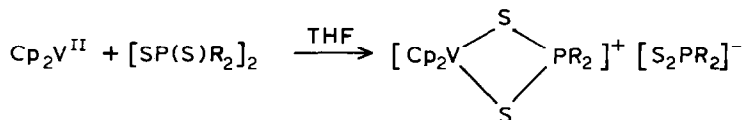
In previous papers [1,2] we have described the various types of behaviour displayed by the ligands bis(dialkylphosphorothionyl) disulphide  $[\text{R}_2\text{P}(\text{S})\text{S}]_2$  ( $\text{R} = \text{Et}, \text{OEt}$  and  $\text{OPr}^i$ ). With  $\text{TiX}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{VOCl}_3$  they react without structural change to give the corresponding complexes  $\text{TiX}_4[\text{R}_2\text{P}(\text{S})\text{S}]_2$  and  $\text{VOCl}_2[\text{R}_2\text{P}(\text{S})\text{S}]_2$  [1]. However, the disulphides react with the bis(cyclopentadienyl- $\mu$ -dicarbonyl)iron,  $[(\eta\text{-Cp}^*\text{Fe}(\text{CO})_2)_2]$ , by oxidative cleavage of the Fe–Fe bond accompanied by homolytic cleavage of the S–S bond of the disulphide ligands, which leads to formation of the dithiophosphate complexes  $\eta\text{-Cp}^*\text{Fe}(\text{CO})_2(\eta^1\text{-SP}(\text{S})\text{R}_2)$ , in which the ligand  $\text{SP}(\text{S})\text{R}_2$  is bonded to iron in monodentate mode.

In this paper the behaviour of these ligands towards vanadocene is described. In these reactions an oxidative addition to  $\text{Cp}_2\text{V}$  takes place, and stable complexes of  $\text{V}^{\text{IV}}$  are obtained. On the basis of analytical, spectroscopic and conductimetric data, the compounds can be formulated as ionic species such as  $[(\eta\text{-Cp})_2\text{V}(\text{S}_2\text{PR}_2)]^+ [\text{S}_2\text{PR}_2]^-$  in which the dithiophosphate ligands can display two distinct modes of coordination, bidentate and ionic. Similar ionic complexes with dithiocarbamate

and xanthate ligands  $[\text{Cp}_2\text{V}(\text{S}_2\text{CNR}_2)]^+$  have been obtained previously [3] by a different method (involving reaction of a different starting material,  $\text{Cp}_2\text{VCl}_2$ , which has vanadium in oxidation state IV) with the sodium salt of the corresponding dithiocarbamate, xanthate, or dithiophosphate.

## Results and discussion

The cyclopentadienyl dithiophosphate or dithiophosphinate vanadium complexes mentioned above can be readily obtained by addition of a THF solution of the corresponding disulphide  $[\text{SP}(\text{S})\text{R}_2]_2$  ( $\text{R} = \text{Et}, \text{OEt}$  and  $\text{OPr}^i$ ) to similar solutions of vanadocene under an inert atmosphere at room temperature. Green solids immediately separate out, which are air stable. The yields are always quantitative. The obtained compounds are 1/1 electrolytes in nitromethane. The reactions can be represented by the following equation:



In this reaction the S-S bond of the disulphide is cleaved in an oxidative addition reaction to vanadocene, the dithiophosphate or dithiophosphinate ligand becoming coordinated to the vanadium atom in bidentate form.

The IR spectra of the product complexes show the characteristic bands of the  $\eta\text{-C}_5\text{H}_5$  rings at 3120–3010m, 1445–1400m, 1300–1250m, 1040m, 860–830vs  $\text{cm}^{-1}$  [4], although some of these are masked owing to the presence of the dithiophosphate ligands, which give strong stretching bands in the range 1065–905  $\text{cm}^{-1}$ ,  $\nu(\text{P}(\text{O})\text{C})$ ; 875–730  $\text{cm}^{-1}$ ,  $\nu(\text{P}-\text{O}(\text{C}))$  and 1240–1080  $\text{cm}^{-1}$   $\delta(\text{CC})$  [5,6].

Similarly, in the case of the complex with dithiophosphinate there are bands at 1013m, 765s, 740s and 706s, which are assigned to the  $\nu(\text{CC})$ ,  $\rho_r(\text{CH}_2, \text{CH}_3)$  and  $\nu(\text{PC})$  vibrations. The bands corresponding to the  $\nu(\text{PS})$  stretching vibrations of the coordinate either bidentate or ionic ligands are observed at 669vs, 596m and 487s  $\text{cm}^{-1}$  for the complex  $[\text{Cp}_2\text{V}(\text{S}_2\text{PEt}_2)_2][\text{S}_2\text{PEt}_2]$  and 730w, 641vs, 570w, 540w and 500 m  $\text{cm}^{-1}$  for  $[\text{Cp}_2\text{V}(\text{S}_2\text{P}(\text{OR})_2)_2][\text{S}_2\text{P}(\text{OR})_2]$  ( $\text{R} = \text{Et}, \text{Pr}^i$ ) [7–9].

Figure 1 shows the EPR spectrum of a solution of  $[\text{Cp}_2\text{V}(\text{S}_2\text{PEt}_2)_2][\text{S}_2\text{PEt}_2]$  at room temperature; it is made up of a superposition of two eight line spectra. These eight lines are due to the coupling of the 3d unpaired electron with the  $^{51}\text{V}$  nucleus ( $I = 7/2$ ), which indicates the presence of paramagnetic species of  $\text{V}^{\text{IV}}$ . Furthermore, each of these lines is split in two components owing to the superhyperfine coupling of the 3d electron with only one atom of  $^{31}\text{P}$  ( $I = \frac{1}{2}$ ) of the dithiophosphate or dithiophosphinate ligand. This confirms that only one dithiophosphate or dithiophosphinate ligand is coordinated to the vanadium atom in bidentate form, the other remaining ionic.

The spectrum can be interpreted by use of the following isotropic spin Hamiltonian:

$$H = g_{\text{iso}}\beta H S + A_{\text{V}} S I + a_{\text{P}} S I_{\text{P}} \quad (1)$$

where  $A_{\text{V}}$  and  $a_{\text{P}}$  are the coupling constants of the vanadium and phosphorus nuclei, respectively. The values determined by these parameters are listed in Table 1.

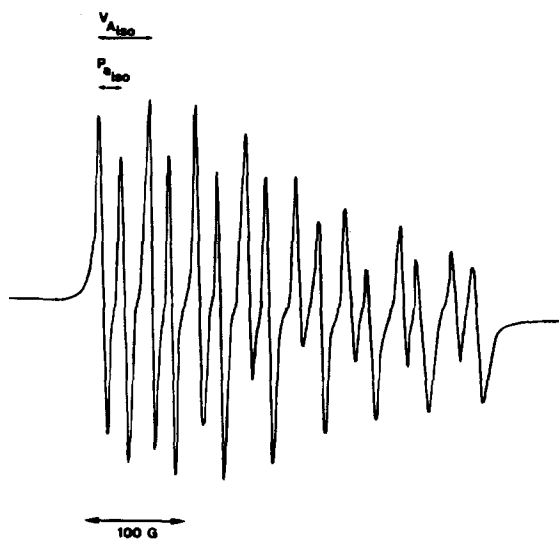


Fig. 1. Room temperature EPR spectrum of  $[\text{Cp}_2\text{V}(\text{S}_2\text{PEt}_2)][\text{S}_2\text{PEt}_2]$  in  $\text{CH}_2\text{Cl}_2$  solution.

The anisotropic spectra recorded in frozen solutions ( $\text{CH}_2\text{Cl}_2$ : toluene) at  $-160^\circ\text{C}$  (Fig. 2) show hyperfine and superhyperfines lines due to the coupling of the unpaired electron with the nuclei of  $^{51}\text{V}$  and  $^{31}\text{P}$ . Two groups of well defined hyperfine signals are observed, and one less well defined third set whose  $g$  and  $A$  values can be calculated from the following relations:  $g_{\text{iso}} = \frac{1}{3}(g_x + g_y + g_z)$  and  $A_{\text{iso}} = \frac{1}{3}(A_x + A_y + A_z)$ .

These spectra can be interpreted by using the following spin Hamiltonian:

$$H = g_z \beta H_z S_z + g_x \beta H_x S_x + g_y \beta H_y S_y + A_z^{\text{V}} S_z I_z + A_x^{\text{V}} S_x I_x + A_y^{\text{V}} S_y I_y + a_z^{\text{P}} S_z i_z + a_x^{\text{P}} S_x i_x + a_y^{\text{P}} S_y i_y \quad (2)$$

The spectrum is analysed on the assumption that the  $[\text{Cp}_2\text{V}(\text{S}_2\text{PR}_2)]^+$  species are pseudotetrahedral with  $C_{2v}$  symmetry, with the  $Z$  axis directed in the  $\text{V}-\text{P}$  direction.

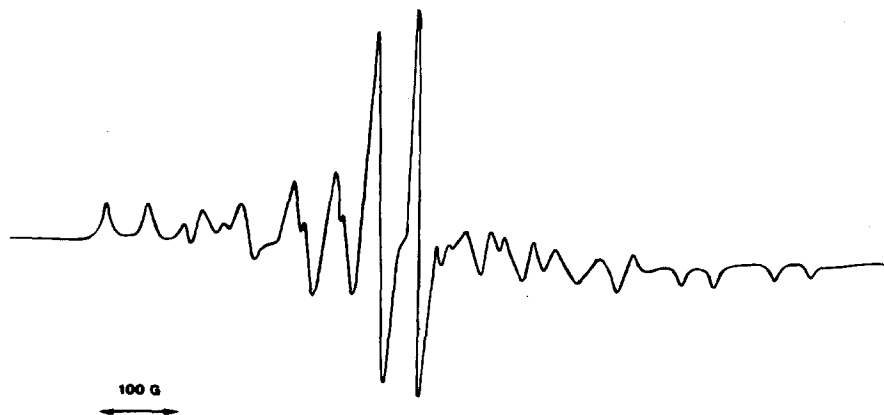


Fig. 2. EPR spectrum of  $[\text{Cp}_2\text{V}(\text{S}_2\text{PEt}_2)][\text{S}_2\text{PEt}_2]$  in  $\text{CH}_2\text{Cl}_2$ /toluene glass at  $-160^\circ\text{C}$ .

TABLE 1

EPR PARAMETERS FOR THE NEW COMPLEXES (the hyperfine coupling,  $-kP$  and  $P$  in units of  $\text{cm}^{-1}$ )<sup>a</sup>

Parameter	$[\text{Cp}_2\text{V}(\text{S}_2\text{PEt}_2)]^+$	$[\text{Cp}_2\text{V}(\text{S}_2\text{P}(\text{OPr}^i)_2)]^+$	$[\text{Cp}_2\text{V}(\text{S}_2\text{P}(\text{OEt})_2)]^+$
$g_x$	1.992	1.980	1.986
$g_y$	1.969	1.970	1.971
$g_z$	2.002	2.001	2.000
$g_{\text{iso}}$	1.994	1.990	1.990
$-\text{}^V A_x$	0.0070	0.0071	0.0070
$-\text{}^V A_y$	0.0120	0.0116	0.0115
$-\text{}^V A_z$	0.0012	0.0014	0.0014
$\text{}^V A_{\text{iso}}$	0.0062	0.0060	0.0060
$\text{}^P a_x$	0.0027	0.0041	0.0040
$\text{}^P a_y$	0.0027	0.0040	0.0040
$\text{}^P a_z$	0.0026	0.0040	0.0041
$\text{}^P a_{\text{iso}}$	0.0028	0.0042	0.0041
$a^2$	0.94	0.094	0.94
$b^2$	0.06	0.06	0.06
$-kP$	0.0063	0.0061	0.0060
$P$	0.0101	0.0093	0.0093

<sup>a</sup> Cp =  $\eta\text{-C}_5\text{H}_5$ .

The values of the  $g$ ,  $\text{}^V A$  and  $\text{}^P a$  parameters of the spin Hamiltonian (eq. 2) are listed in Table 1. The data show that there are no significant changes in the values of these parameters for the two dithiophosphate ligands used, which indicates that the alkyl groups of these ligands have no important influence on the electronic properties of the compounds. However, when an alkoxide group of the complex involving dithiophosphate is replaced by an alkyl group in the complex involving dithiophosphinate, there is a significant reduction in the  $^{31}\text{P}$ -superhyperfine splitting. This effect will be discussed later.

The values obtained for  $g_x$ ,  $g_y$ ,  $g_z$ ,  $g_e$  (Table 1) indicate, in agreement with observations by Stewart and Porte [10], that the ground state represented by  $|\psi_0\rangle = a|d_{z^2}\rangle + b|d_{x^2-y^2}\rangle$  is predominantly  $d_{z^2}$ . It is of interest that in similar niobium compounds, such as  $[\text{Cp}_2\text{Nb}(\text{S}_2\text{P}(\text{OR})_2)]\text{PF}_6$ , the unpaired electron has been shown to be in a  $d_{x^2-y^2}$  orbital [11].

The values of  $a$ ,  $b$ ,  $P$  and  $K$  can be calculated from the Evans equations [12]. From the values of  $a^2$  and  $b^2$  we conclude that the unpaired electron is largely in a  $d_{z^2}$  orbital. The values of  $P$  are in the range  $93\text{--}101 \times 10^{-4} \text{ cm}^{-1}$ , which by comparison with the  $P$  value for the  $\text{V}^{4+}$  ion ( $172 \times 10^{-4} \text{ cm}^{-1}$ ), indicate that the electron is about 54–58% located in the metal, and for thus there is a strong delocalization between the ligands. The  $P$  values indicated in Table 1 show a stronger delocalization in the complexes containing dithiophosphate than in those containing dithiophosphinate, in agreement with the higher value of  $\text{}^P a_{\text{iso}}$  in the dithiophosphates. Furthermore these  $P$  values are in agreement with those obtained for other vanadium complexes containing four members sulphur chelates [13].

The splitting of the hyperfine lines observed in the EPR spectra (Fig. 1), and the values of  $\text{}^P a_{\text{iso}}$  (Table 1), indicate that there is a strong superhyperfine coupling of the unpaired  $3d$  electron with the  $^{31}\text{P}$  nucleus of the sulphur ligand. The  $\text{}^P a$  values

listed in Table 1 show that the superhyperfine tensor is isotropic, which suggests that the orbital of  $^{31}\text{P}$  involved in this interaction is predominantly of "s" character.

In the species under study namely,  $[\text{Cp}_2\text{V}(\text{S}_2\text{PR}_2)]^+$  ( $\text{R} = \text{Et}, \text{OEt}, \text{OPr}^i$ ) with pseudotetrahedral symmetry.  $C_{2v}$ , and ground state essentially  $d_{z^2}$ , as we have already indicated, the vanadium  $d_{z^2}$  orbital and the  $3s$  orbital of the transannular P-atom belong to the same type of symmetry in the  $C_{2v}$  group, making possible the observation of the superhyperfine coupling [14].

The  $^{31}\text{P}$  isotropic coupling is given by the following expression [15]:

$$P_a = \frac{8\pi}{3} g_e g_n \beta_e \beta_n |\psi_{3s}(O)|^2 C_s^2$$

where  $C_s$  is the coefficient of the phosphorus  $3s$  orbital in the molecular orbital which contains the unpaired electron and  $|\psi_{3s}(O)|^2$  is the electronic density of the nucleus. The ( $C_s$ ) coefficient is calculated by the relation between the  $^{31}\text{P}$  superhyperfine isotropic splitting,  $^{\text{P}}a_{\text{obs}}$ , and that calculated for one unpaired electron in a  $3s$  orbital of phosphorus,  $^{\text{P}}a_{\text{calcd}}$ :

$$|C_s|^2 = \frac{^{\text{P}}a_{\text{obsd.}}}{^{\text{P}}a_{\text{calcd.}}} = \frac{^{\text{P}}a_{\text{obsd.}}}{3640 \text{ (gauss)}}$$

From this equation a  $|C_s|^2$  value of 0.0082 can be derived for the dithiophosphate complex  $[\text{Cp}_2\text{V}(\text{S}_2\text{PEt})_2]^+ [\text{S}_2\text{PEt}_2]^-$  and values of 0.0123 and 0.0120 for the dithiophosphate complexes  $[\text{Cp}_2\text{V}(\text{S}_2\text{P}(\text{OR})_2)]^+ [\text{S}_2\text{P}(\text{OR})_2]^-$  ( $\text{R} = \text{Et}, \text{Pr}^i$ ), respectively.

This appreciable difference between the  $|C_s|^2$  coefficients, which is in agreement with the observed difference between the  $^{\text{P}}a_{\text{iso}}$  values (Table 1), can be attributed to the difference in the amount of  $s$ -character in the P-S bond of the dithiophosphate and dithiophosphinate ligands. In the dithiophosphate ligands, the P-S bond is shorter and has a higher  $s$ -character than in the dithiophosphinate complexes as shown by the IR and X-ray crystallographic data [16,17]; for this reason the  $^{31}\text{P}$ -superhyperfine coupling in the dithiophosphates is stronger than in the dithiophosphinates. Similar observations have been made for vanadyl complexes containing this type of ligands [18].

## Experimental

All reactions were carried out under oxygen-free  $\text{N}_2$  using Schlenk techniques. The disulphides  $[\text{SP}(\text{S})(\text{OR})_2]_2$  ( $\text{R} = \text{Et}, \text{Pr}^i$ ) were prepared by oxidation of the  $(\text{RO})_2\text{P}(\text{S})\text{SNa}$  precursor with  $\text{I}_2$  [19], and  $[\text{SP}(\text{S})\text{Et}_2]_2$  was prepared by Kucken's method [20].  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$  was prepared by a published method [21]. The IR spectra were recorded at  $4000\text{--}200 \text{ cm}^{-1}$  on a Nicolet 5DX FT-IR spectrophotometer using Nujol and Hostafion mulls between CsI windows.

The EPR spectra were recorded on a Varian E-12 spectrometer at a microwave frequency of 9 GHz (X-band) equipped with a HP5342A frequency-meter and a Bruker NMR gaussmeter.

The conductivity measurement was carried out on nitromethane solutions with a Metrohm Conductometer E-518.

TABLE 2  
EXPERIMENTAL AND ANALYTICAL DATA FOR THE COMPLEXES

Complex	$(\eta\text{-C}_5\text{H}_5)_2\text{V}$ (g(mmol))	Disulphide (g(mmol))	Analysis (Found (calcd.)(%))		
			C	H	V
$[\text{Cp}_2\text{V}(\text{S}_2\text{PEt}_2)]_2[\text{S}_2\text{PEt}_2]$	1 (2.9)	0.98 (3.2)	44.0 (44.3)	5.9 (6.1)	10.1 (10.5)
$[\text{Cp}_2\text{V}(\text{S}_2\text{P}(\text{OEt})_2)]_2[\text{S}_2\text{P}(\text{OEt})_2]$	1 (2.9)	1.20 (3.2)	38.8 (39.2)	5.1 (5.4)	9.0 (9.3)
$[\text{Cp}_2\text{V}(\text{S}_2\text{P}(\text{O Pr}^i)_2)]_2[\text{S}_2\text{P}(\text{O Pr}^i)_2]$	1 (2.9)	1.36 (3.2)	43.2 (43.5)	5.9 (6.2)	8.1 (8.4)

#### Preparation of compounds

$[(\eta\text{-C}_5\text{H}_5)_2\text{V}(\text{S}_2\text{PEt}_2)]_2[\text{S}_2\text{PEt}_2]$ . A solution of  $[\text{SP}(\text{S})\text{Et}_2]_2$  (0.98 g, 3.2 mmol) in 10 ml of THF was added dropwise to a solution of freshly sublimed  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$  (1 g, 2.9 mmol) in THF (40 ml) saturated with oxygen-free  $\text{N}_2$ . A green solid immediately appeared, and this was filtered off, washed several times with THF, and dried in vacuo. The yield was 80% based on the  $(\eta\text{-C}_5\text{H}_5)_2\text{V}$  taken.

Detail of the preparation of the other complexes are given in Table 2.

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