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ELECTRON PARAMAGNETIC RESONANCE LINEWIDTH STUDIES OF (π -C₅H₅)₂TaCl₂, (π -C₅H₅)₂NbCl₂ AND (π -C₅H₅)₂VCl₂ COMPLEXES

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Summary

The electron paramagnetic relaxation phenomena of (π -C₅H₅)₂TaCl₂, (π -C₅H₅)₂NbCl₂ and (π -C₅H₅)₂VCl₂ in dilute chloroform solutions have been investigated. This has enabled the separate contributions to the observed EPR linewidths from spin-rotational interaction, *g*-tensor anisotropy, hyperfine coupling anisotropy, and unresolved chlorine hyperfine coupling to be evaluated. These results have been used to estimate the size of the chlorine isotropic hyperfine coupling constants and thus the extent of delocalisation of the unpaired electron on to the chlorine ligands.

Introduction

In a previous study of the EPR spectra of (π -C₅H₅)₂TaCl₂, it was found [1] that the unpaired electron in the complex lies essentially in the $5d_{x^2-y^2}$ metal-ion orbital and is extensively delocalised (15%) on to the chlorine ligands. On the other hand, the unpaired electron in the complexes (π -C₅H₅)₂NbCl₂ and (π -C₅H₅)₂VCl₂ lies [2–4] 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. This kind of information was obtained from the analysis of the spin-dipolar interaction of the magnetic moment of the unpaired electron with the magnetic moment of the metal nucleus.

It is possible to obtain similar information about the delocalisation of the unpaired electron on to the chlorine ligands from the size of the chlorine nuclear hyperfine interaction in these complexes. We were not able to resolve chlorine hyperfine coupling in the EPR spectra due to the interaction of the unpaired electron with the chlorine ligand nuclei. However, it is still possible to estimate the size of the isotropic hyperfine coupling from the contribution which it makes to the width of the lines in the EPR spectra of these complexes in solution. It was therefore decided to analyse in detail the EPR linewidths of

TABLE 1
 SPIN-HAMILTONIAN PARAMETERS FOR TANTALUM, NIOBIUM AND VANADIUM COMPLEXES IN CHLOROFORM ^a

Complex	g_x	g_y	g_z	g_0	A_x	A_y	A_z	A_0
$(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$	1.9850	1.9829	1.9889	1.9689	-1.309	-1.338	-3.426	-2.024
$(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$	1.9800	1.9400	2.0000	1.9733	-2.009	-3.011	-0.995	-2.005
$(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$	1.9860	1.9710	2.000	1.9857	-1.394	-2.205	-0.286	-1.295

^a All hyperfine tensor components are in units of 10^9 rads s^{-1} . Limits of error in the principal components of g and A are ± 0.0007 and ± 0.02 , respectively.

these complexes as a function of temperature in order to separate the unresolved ligand hyperfine structure contribution from the various other effects which contribute to the linewidths. The estimated values of the chlorine hyperfine coupling obtained in this way are then used to independently estimate the extent of delocalisation of the unpaired electron into the chlorine ligand orbitals.

Experimental

The EPR spectra were recorded on a Varian E-109 spectrometer equipped with a Varian E-257 temperature control accessory and the temperature was measured with a copper constantan thermocouple.

The complexes of tantalum [5] niobium [5] and vanadium [6] were prepared and purified according to literature methods and the linewidths of each complex in chloroform were measured as a function of temperature. The chloroform solvent, was repeatedly fractionated and purified with P_2O_5 , and the dissolved oxygen was removed by degassing involving repeated freezing and thawing of the solution.

The viscosity coefficients η of chloroform as a function of temperature were taken from the International Critical Tables [7]. The values for low temperatures were obtained by extrapolation, using the formula given in the tables.

In order to keep intermolecular interactions from affecting the linewidths of the EPR spectrum, the concentrations were reduced until no further narrowing was observed as a function of concentration. This was achieved at $10^{-3} M$.

The widths of the individual spectral lines were determined by measuring the heights of the lines on a broad sweep and the width of the sharpest line on a narrower sweep. The lines were assumed to be of Lorentzian shape so that the height, H , and the width, W , were related through the familiar relationship, $C = HW^2$, where C is a constant for a given spectrum and can be determined from the height and width of the sharpest line. Preliminary investigation indicated that the influence of the line overlap on the measured linewidths was negligible even at low temperatures so that no correction for overlapping of lines was required.

Analysis of EPR spectra

The components of the electronic Zeeman interaction and the hyperfine coupling tensors for each complex were obtained from analysis of the EPR spectra of the complexes in liquid and solid solutions. The values of these components are given in Table 1 and agree well with our previous results [1] for a tantalum complex and with those reported by Stewart and Porte [3] for niobium and vanadium complexes. Typical EPR spectra for a tantalum complex recorded at room temperature and at 77 K are shown in Figure 1 and 2, respectively.

The peak-to-peak width ΔH of the hyperfine lines depend on the nuclear spin quantum number, m_I , and can be expressed by the cubic equation [8,9].

$$\Delta H = \alpha + \alpha' + \alpha'' + \beta m_I + \gamma m_I^2 + \delta m_I^3 \dots \quad (1)$$

The parameter α' of this equation arises from modulation of both anisotropic

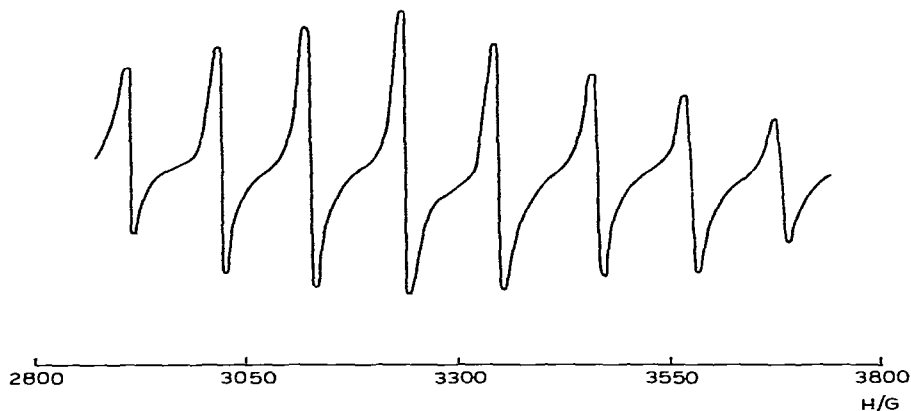


Fig. 1. EPR spectrum of 10^{-3} M solution of $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$ in chloroform at 298 K.

g and hyperfine tensors; β from a cross correlation between these two; γ and δ from modulation of the anisotropic hyperfine tensor; α'' from the spin-rotational interaction; and α from the unresolved hyperfine coupling, plus any other small contributions which have not been considered above. Theoretical expressions for the parameters α' , β , γ and δ were described by Wilson and Kivelson [9,10] and reproduced by Chasteen and Hanna [11].

Results and discussion

In order to estimate the values of the isotropic ligand hyperfine coupling, it is necessary to calculate all the other contributions to the linewidths of the EPR spectra. To do this, the linewidths of the EPR spectra are fitted to the polynomial formula 1 using a least squares procedure and the parameters $\alpha + \alpha' + \alpha''$, β , γ , and δ are obtained. The values of these parameters at different temperatures for each complex are listed in Tables 2, 3 and 4.

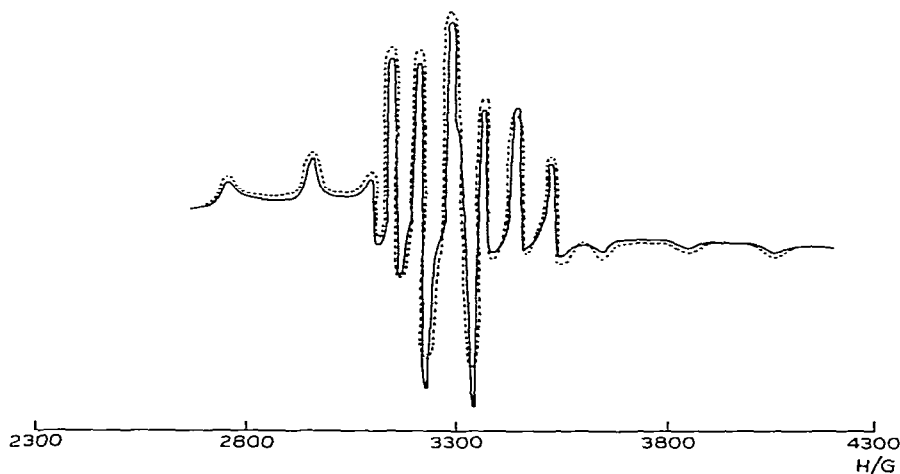


Fig. 2. Observed (full line) and calculated (dotted line) EPR spectra of 10^{-3} M solution of $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$ in chloroform at 77 K.

TABLE 2

LINEWIDTH PARAMETERS FOR $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$ IN CHLOROFORM AT VARIOUS TEMPERATURES

Temp (K)	$\alpha + \alpha' + \alpha''$ (G)	β (G)	γ (G)	δ (G)	τ_R (10^{-11} s rad $^{-1}$)	r (Å)
330	27.13	1.20	0.57	-0.016	4.4	4.88
320	27.20	1.18	0.65	-0.002	5.0	4.89
308	27.50	1.24	0.72	0.009	5.9	4.86
297	28.00	1.42	0.85	0.011	6.7	4.86
280	29.25	2.20	1.00	-0.035	8.5	4.92
270	32.40	2.10	1.21	0.014	9.7	4.92
262	33.45	3.28	1.40	-0.092	10.0	4.99
253	37.00	6.20	1.50	-0.270	14.0	5.24

According to the Kivelson linewidth theory [9], the values of γ are usually more precise than the values of β . By using the values of γ at each temperature and the spin-Hamiltonian parameters of Table 1, the rotational correlation times, τ_R , can be calculated from equation 13 given in reference 11. The values of τ_R are then used to calculate α' from equation 10 given in the same reference. Thus the values of the residual linewidth $\alpha + \alpha''$, could then be calculated, since the values of $\alpha + \alpha' + \alpha''$ were already known. The values of τ_R and the effective molecular radius, r , obtained from equation 15 in reference 11, are listed in Tables 2, 3 and 4.

Since values of α'' are proportional to T/η , the contribution of the ligand hyperfine structure, α , to the linewidth can be obtained by plotting $\alpha + \alpha''$ vs. T/η . The various plots of $\alpha + \alpha''$ vs. T/η for tantalum, niobium, and vanadium complexes are shown in Figures 3, 4 and 5 respectively. As shown in the Figures, the contributions to the linewidths from unresolved ligand hyperfine structures are 14.4, 4.8 and 3.1 gauss for $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$, respectively.

Since the experimental results [1,12,13] and Molecular Orbital calculations [3] indicate that the interaction of the unpaired electron with proton nuclei of the cyclopentadiene rings is very small in the tantalum, niobium and vanadium complexes, the unresolved hyperfine structure may be attributed to the chlorine ligands.

Each of the lines in the EPR spectra of these complexes consists of an un-

TABLE 3

LINEWIDTH PARAMETERS FOR $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$ IN CHLOROFORM AT VARIOUS TEMPERATURES

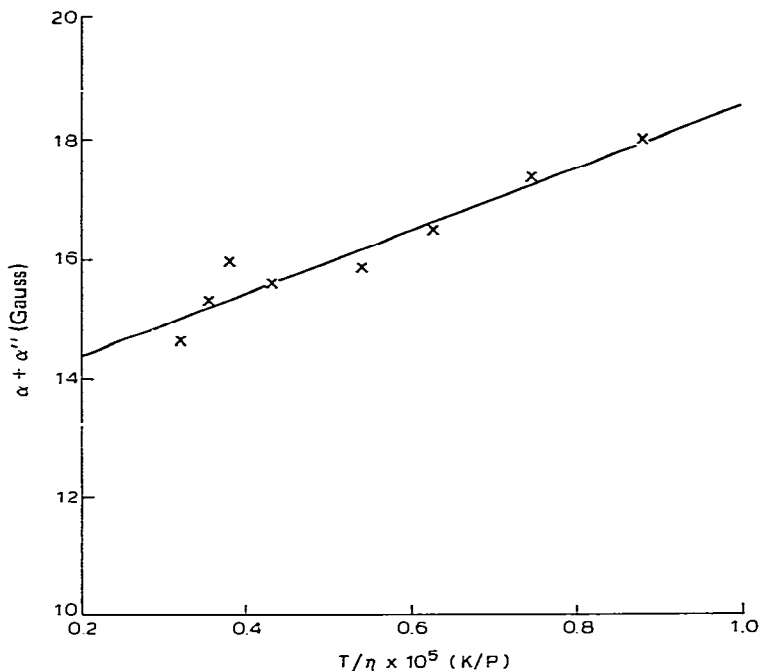
Temp (K)	$\alpha + \alpha' + \alpha''$ (G)	β (G)	γ (G)	δ (G)	τ_R (10^{-13} s rad $^{-1}$)	r (Å)
332	12.90	0.27	0.01	-0.001	5.9	1.18
325	12.20	0.36	0.03	-0.006	13.0	1.49
316	12.80	0.37	0.06	-0.001	26.0	1.79
303	11.13	0.44	0.09	-0.001	40.0	1.94
293	11.30	0.53	0.12	-0.001	56.0	2.09
290	11.12	0.24	0.13	0.020	60.0	2.12
285	11.0	0.56	0.15	0.002	69.0	2.16
273	11.3	0.70	0.20	0.003	90.0	2.26

TABLE 4

LINEWIDTH PARAMETERS FOR $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$ IN CHLOROFORM AT VARIOUS TEMPERATURES

Temp (K)	$\alpha + \alpha' + \alpha''$ (G)	β (G)	γ (G)	δ (G)	τ_R (10^{-12} s rad^{-1})	r (Å)
320	6.13	0.32	0.07	-0.013	6.6	2.49
308	6.24	0.36	0.08	-0.014	7.5	2.45
300	5.34	0.44	0.10	-0.022	8.7	2.48
285	5.40	0.45	0.12	-0.016	10.0	2.48
270	6.58	0.46	0.16	-0.003	12.0	2.52
257	6.85	0.50	0.19	-0.002	15.0	2.56
254	6.95	0.52	0.21	-0.003	17.0	2.61
232	8.50	0.66	0.50	0.034	37.0	3.18

resolved 1 : 2 : 3 : 4 : 3 : 2 : 1 multiplet, and so to estimate the value of the chlorine hyperfine coupling which would give rise to a particular contribution to the linewidths, a computer programme has been used to plot out the single line arising from the superposition of the seven peaks of this type. The spacing between the constituent peaks was simply varied until the width of the single composite line was larger than that of the constituent lines by 14.4, 4.8, and 3.1 gauss for $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$, respectively. In this way the chlorine nuclear hyperfine couplings were estimated to be 12, 4 and 2.5 gauss for $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$, respectively. These values were then used to estimate the extent of delocalization of the unpaired electron in the complexes on the chlorine ligands.

Fig. 3. $\alpha + \alpha''$ vs T/η for $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$ in chloroform.

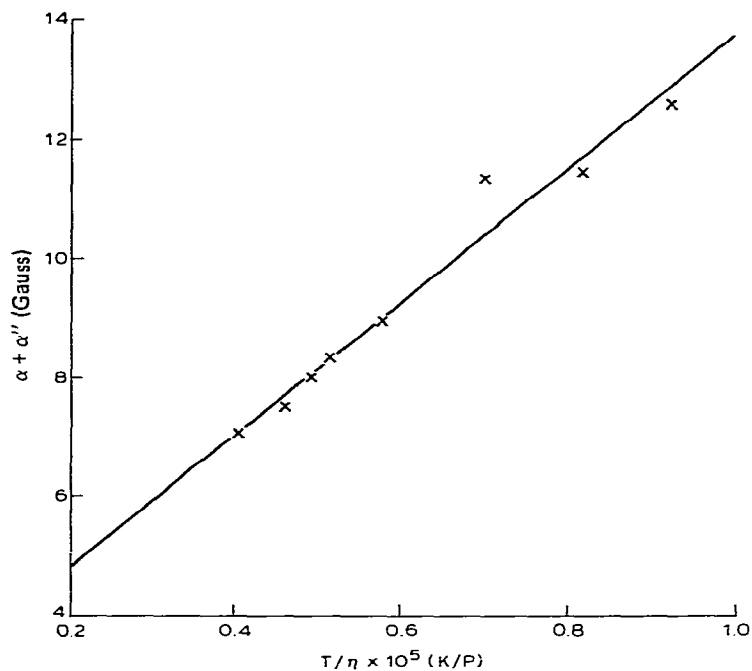


Fig. 4. $\alpha + \alpha''$ vs T/η for $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$ in chloroform.

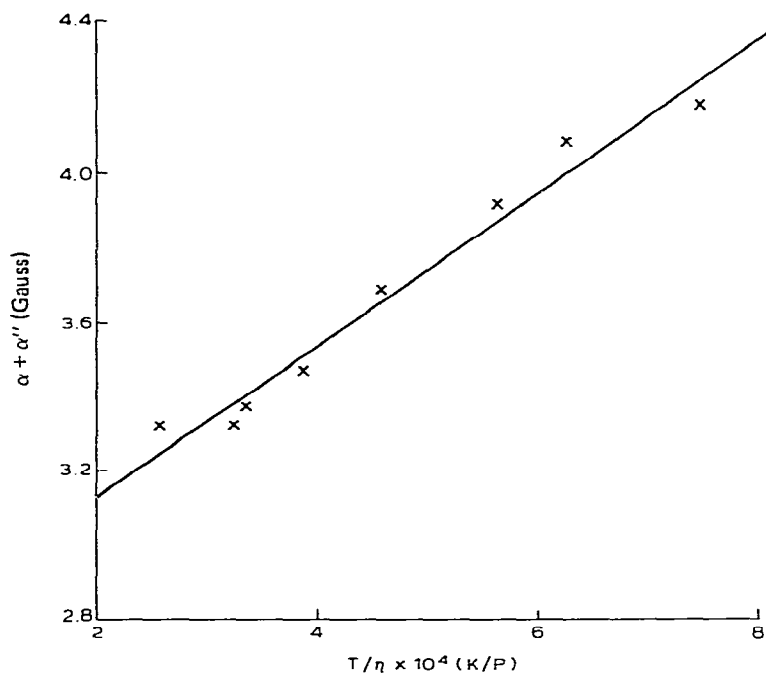


Fig. 5. $\alpha + \alpha''$ vs T/η for $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$ in chloroform.

By setting the values of the chlorine isotropic coupling constant roughly equal to the largest principal value of the chlorine spin-dipolar interaction $4/7 p(\alpha^{*(1)})^2$, where $(\alpha^{*(1)})^2$ is the coefficient of the chlorine p -orbital in the molecular orbital containing the unpaired electron, and $4/7 p$ is the largest principal value of the spin-dipolar interaction for one electron in a chlorine p -orbital, which is estimated to be 90 gauss [14–16], the values of $(\alpha^{*(1)})^2$ were estimated to be 0.13, 0.04, and 0.03 for $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$, respectively. Thus the linewidth analysis of these complexes confirms that the unpaired electron is in metal orbitals and delocalised by about 13%, 4%, and 3% on to the chlorine ligands of $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$, and $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$, respectively, in close agreement with the results reached from the analysis of the spin-Hamiltonian parameters [1,3]. In addition these results also confirm that the unpaired electron is extensively delocalised on to the chlorine ligands in $(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_2$, and slightly delocalised on to these ligands in $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$.

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