Electron Spin Resonance Studies † on Bis(chloroalkoxy)-bis(η-cyclopentadienyl)vanadium(IV) Complexes

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The e.s.r. spectra of [V(OCH$_2$CH$_2$Cl)$_2$(η-C$_5$H$_5$)$_2$] and [V(OCHMeCH$_2$Cl)$_2$(η-C$_5$H$_5$)$_2$] were determined at room temperature and as frozen solutions at 120 K. From $g_x = 1.985$, $g_y = 1.975$, and $g_z = 2.002$ and (^{51}V) $A_x = -77$, $A_y = -125$, $A_z = -17$ G, the molecular coefficients of the a_1 ground state and the usual e.s.r. parameters χ, P, K, $\langle r^{-3}\rangle$, and ξ were calculated and compared with the literature data for related [VX$_2$(η-C$_5$H$_5$)$_2$] (X=Cl, Et, or OCN) derivatives. The importance of the role of the solvent on spectral features has been demonstrated.

Alkoxide derivatives of vanadium(IV) are poorly documented and e.s.r. studies are limited to tetra-t-butoxyvanadium by Kokoszka *et al.*[1] In bis(η-cyclopentadienyl)vanadium(IV) chemistry a wide variety of complexes [VX$_2$(η-C$_5$H$_5$)$_2$] (X = Cl, SCN, OCN, *etc.*) have been explored [2] but conventional methods of obtaining [V(OR)$_2$(η-C$_5$H$_5$)$_2$] (R = alkyl) failed. In a previous study,[3] one of us reported that bis(chloroalkoxy)-bis(η-cyclopentadienyl)vanadium complexes are readily obtained by insertion of oxirane into the vanadium–chlorine bonds of [VCl$_2$(η-C$_5$H$_5$)$_2$]. In this work, we have studied the e.s.r. spectra of [V(OCH$_2$CH$_2$Cl)$_2$(η-C$_5$H$_5$)$_2$] (1) and [V(OCH-MeCH$_2$Cl)$_2$(η-C$_5$H$_5$)$_2$] (2) in solution at room temperature and in frozen solution at 120 K.

Results and Discussion

At room temperature, the spectra of the derivatives (1) and (2) obtained either in dichloromethane or in pentane solution show the eight lines expected for the hyperfine interaction of the unpaired electron with the ^{51}V nucleus (99.8% abundance; $I = \frac{7}{2}$). They closely resemble those of [VCl$_2$(η-C$_5$H$_5$)$_2$].

On cooling the CH$_2$Cl$_2$ solution of (1) to 120 K, the *X*-band and *Q*-band spectra consist of three overlapping sets of eight lines as shown in Figure 1. The main spectral features compare well with other [VX$_2$(η-C$_5$H$_5$)$_2$] complexes of C_{2v} symmetry.[2] Thus the same axial reference frame can be assumed as was determined by Petersen and Dahl.[4]

Because of the overlapping of lines in the central region of the spectrum, good values for g_z and A_z are difficult to obtain; so from the experimental spectra initial values of g_x,g_y and A_x,A_y could be determined. Values of g_z and A_z were deduced from the equations $3A_{\text{iso.}} = A_x + A_y + A_z$ and $3g_{\text{iso.}} = g_x + g_y + g_z$. Using these six parameters, the computed spectrum (for *X*-band) was obtained in good agreement with the experimental one. The simulation can only be achieved by taking into account Gaussian and Lorentzian broadening (20% Gaussian, width at half-height 40 G; 80% Lorentzian, width at half-height 10 G).[5] All the values are reported in the Table and the calculated spectrum is shown in Figure 1.

The CH$_2$Cl$_2$ frozen solution of compound (2) gives the same spectrum and parameters.

Based on the same ligand-field model previously employed by Petersen and Dahl to interpret the e.s.r. data for [VS$_5$(η-C$_5$H$_5$)$_2$] [6] and [VCl$_2$(η-C$_5$H$_4$Me)$_2$],[4] the metal orbital character of the unpaired electron has been deduced from the hyperfine coupling parameters. The mixing coefficients, a and b for the a_1 ground state $|\psi_0\rangle = a|d_{z^2}\rangle + b|d_{x^2-y^2}\rangle$, as well as the corresponding e.s.r. parameters χ, P, K, and $\langle r^{-3}\rangle$ have been calculated using the expressions obtained by Evans *et al.*[7] from second-order perturbation theory by McGarvey.[8] The results are collected in the Table and compared with those previously reported for [VCl$_2$(η-C$_5$H$_5$)$_2$],[2] [VEt$_2$(η-C$_5$H$_5$)$_2$],[7] and [V(OCN)$_2$(η-C$_5$H$_5$)$_2$].[2]

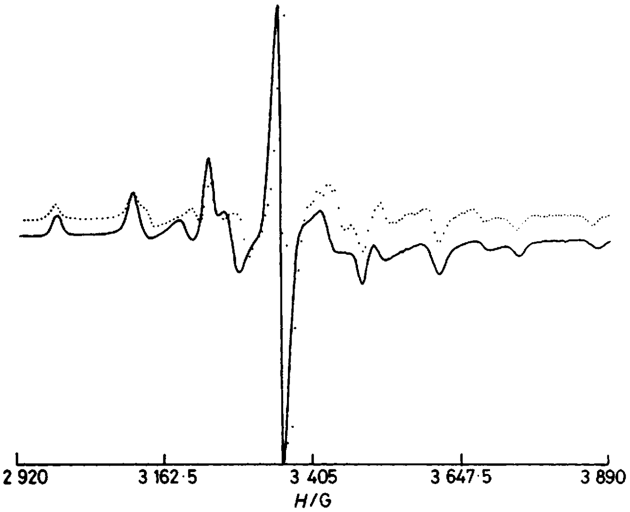

Figure 1. Observed (—) and calculated (· · ·) (not superimposed for clarity) *X*-band e.s.r. spectra of a frozen CH$_2$Cl$_2$ solution of [V(OCH$_2$CH$_2$Cl)$_2$(η-C$_5$H$_5$)$_2$]

The a^2/b^2 ratio, $(-0.973)^2/(0.231)^2 = 17.7$, shows that $|\psi_0\rangle$ is largely composed of d_{z^2} with a small amount of $d_{x^2-y^2}$ character. According to Petersen and Dahl [6] the small positive contribution from the $d_{x^2-y^2}$ orbital represents an increase in the amount of electron density within the X–V–X bond angle of [VX$_2$(η-C$_5$H$_5$)$_2$]. This contribution is of similar importance for X = OCH$_2$CH$_2$Cl, and for X = OCN or Et, and significantly higher for these than for [VCl$_2$(η-C$_5$H$_5$)$_2$].

The value of the spin-polarisation component K is not very different from $A_{\text{iso.}}$ as expected when the value of $g_{\text{iso.}}$ is not very different from 2, since $A_{\text{iso.}} = -K + (g_{\text{iso.}} - 2.0023)P$. The negative value of χ, the contact term, is nearly the same for [V(OCH$_2$CH$_2$Cl)$_2$(η-C$_5$H$_5$)$_2$], [VCl$_2$(η-C$_5$H$_5$)$_2$], and [V(OCN)$_2$(η-C$_5$H$_5$)$_2$], which indicates that the 4*s* character of the unpaired electron is essentially the same for the three

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† *Non-S.I. unit employed*: G = 10^{-4} T.

Table. Spin-Hamiltonian parameters for the metallocene derivatives $[VX_2(\eta\text{-}C_5H_5)_2]$

Compound	$[V(OCH_2CH_2Cl)_2(\eta\text{-}C_5H_5)_2]$	$[VCl_2(\eta\text{-}C_5H_5)_2]$ [a]	$[VEt_2(\eta\text{-}C_5H_5)_2]$ [b]	$[V(OCN)_2(\eta\text{-}C_5H_5)_2]$ [a]
$g_{iso.}$	1.988	1.988	1.995	1.981
$A_{iso.}$/G	−73	−73.5	−62.4	−73.5
g_x	1.985	1.986	1.977	1.985
g_y	1.975	1.971	2.000	1.957
g_z	2.002	2.000	1.993	2.000
A_x/G	−77	−79.2	−67.0	−78.5
A_y/G	−125	−125.2	−108.0	−127.8
A_z/G	−17	−16.3	−13.9	−20.0
a	−0.973	−0.977	−0.972	−0.973
b	0.231	0.213	0.232	0.231
a^2/b^2	17.7	21.0	17.4	17.7
10^4P/cm^{-1}	98.5	101.0	89.2	98.4
K/G	71.5	71.8	61.8	68.3
$\langle r^{-3}\rangle$/a.u.	2.10	2.16	1.91	2.10
χ	−2.14	−2.15	−1.85	−2.19
ξ/cm^{-1}	115	120	100	115

[a] Ref. 2. [b] Ref. 7.

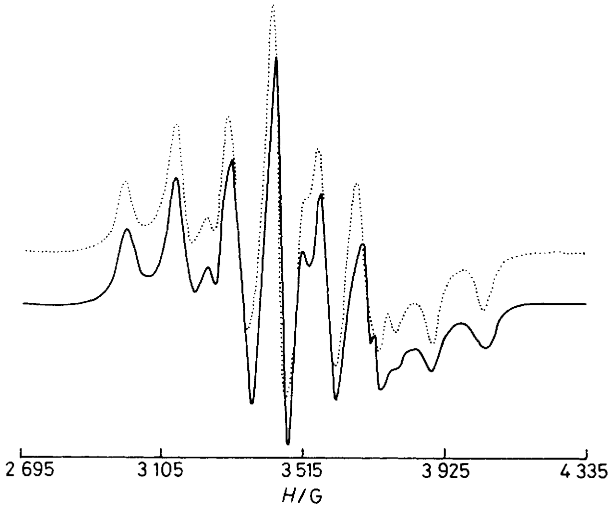

Figure 2. Observed (—) and calculated (· · ·) (not superimposed for clarity) *X*-band e.s.r. spectra of a frozen pentane solution of $[V(OCHMeCH_2Cl)_2(\eta\text{-}C_5H_5)_2]$

compounds (*ca.* 1.3%) and lower than for $[VEt_2(\eta\text{-}C_5H_5)_2]$ (*ca.* 1.9%).

The values of P and $\langle r^{-3}\rangle$ are correlated with the positive charge on the metal and the ionicity of the bonds in the complex. The closeness of the values of these two parameters for $[V(OCH_2CH_2Cl)_2(\eta\text{-}C_5H_5)_2]$ compared to those for $[V(OCN)_2(\eta\text{-}C_5H_5)_2]$ is not unexpected since in both complexes the ligand is oxygen-bonded to the metal. The effective nuclear charge on the vanadium is slightly less than +1.[4]

The metal ion spin–orbit coupling constant ξ was estimated from a curve, obtained by plotting the ξ values calculated by Dunn [9] for various oxidation states of vanadium *versus* the corresponding $\langle r^{-3}\rangle$ values calculated by Goodman and Raynor.[10]

The electronic transitions determined from u.v.–visible absorption spectra are compatible with the above data but no precise comparison with ΔE_{yz}, ΔE_{zx}, and ΔE_{xy} calculated from g_x, g_y, and g_z was made. For example, in the case of compound (1), the values of $\nu_{max.}$ (cm^{-1}) and their assigned transitions are 11 300 (*d–d* transition), 17 240 (*d–d* transition), and 26 000 (charge transfer from C_5H_5 ring to V^{IV}).

Complementary experiments demonstrated the important role of the solvent on the spectral features of frozen solutions. For instance, using CH_2Cl_2 at 120 K, the spectrum of $[VCl_2(\eta\text{-}C_5H_5)_2]$ only consists of one line (g = 1.993) and no hyperfine structure is apparent, in contrast with the eight lines observed at 293 K whatever the solvent ($g_{iso.}$ = 1.993, $A_{iso.}$ = −75 G, in CH_2Cl_2) and with the three sets of eight lines obtained in the literature [2] using a chloroform–ethanol (9 : 1) mixture as solvent. Moreover, changing dichloromethane for pentane does not modify the spectrum of $[V(OCHMeCH_2Cl)_2(\eta\text{-}C_5H_5)_2]$ at room temperature ($g_{iso.}$ = 1.990, $A_{iso.}$ = −74 G, in CH_2Cl_2; $g_{iso.}$ = 1.983, $A_{iso.}$ = −80 G, in C_5H_{12}) but at 120 K the spectrum in pentane is quite different from those generally described for $[VX_2(\eta\text{-}C_5H_5)_2]$ in this work and in the literature (see Figure 2). The previous assignment of the orientation of the principal axes could no longer be used. The parameters g_1 = 1.985, g_2 = 1.957, and g_3 = 1.938, A_1 = −85, A_2 = −145 and A_3 = −25 G, and the simulated spectrum were obtained as indicated above (25% Gaussian, width at half-height 120 G; 75% Lorentzian, width at half-height 30 G).

Experimental

All manipulations were performed under argon. The compounds $[V(OR)_2(\eta\text{-}C_5H_5)_2]$ (R = CH_2CH_2Cl or $CHMeCH_2Cl$) were prepared by reacting the corresponding oxirane with a CH_2Cl_2 solution of $[VCl_2(\eta\text{-}C_5H_5)_2]$ as previously reported.[3] E.s.r. spectra were recorded on a Bruker ER200TT spectrometer equipped with E.I.P. frequencemeter, Bruker n.m.r. Gaussmeter, and Oxford cryostat accessories. U.v. spectra were recorded in CH_2Cl_2 solution on a CARY 14 spectrometer.

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