Electron Spin Resonance Studies of some Bis(cyclopentadienyl) Complexes of Vanadium(IV) and Niobium(IV)

Allan T. Casey and J. Barrie Raynor
Department of Chemistry, The University, Leicester LE1 7RH

40 Complexes of the type $[M(\eta^5-C_5H_5)_2L_2]^{n+}$ (M = V or Nb; L_2 = one bidentate or two unidentate ligands; n = 1 or 0) have been studied by e.s.r. spectroscopy at room temperature and at 77 K. From the g and metal hyperfine tensors, the hyperfine parameter P, the spin-polarisation parameter, κ, and the orbital coefficients a and b were calculated. The unpaired electron is in an orbital of a_1 symmetry comprising $ad_{z^2} + bd_{x^2-y^2}$. Trends in these parameters are related to the interbond angle L–V–L and to the relative π-acceptor and π-donor character of L.

A large number of cyclopentadienyl complexes of d^1 ions have been synthesised and their e.s.r. spectra recorded and analysed.[1–22] Recently the preparation was reported of a number of dithiolate complexes of the bis(η^5-cyclopentadienyl)vanadium(IV) moiety, including a number of dithiocarbamates, xanthates, and dithiophosphates. Some e.s.r. spectra were reported along with spin-Hamiltonian parameters based on the assumption of axial symmetry. Subsequent crystal structure determinations and e.s.r. spectra recorded on a more sensitive spectrometer have shown that such an assumption is not correct.[6] We here present a re-examination of the e.s.r. spectra of these compounds together with results for a number of analogous niobium(IV) complexes.

Experimental

E.s.r. spectra were recorded at *X*-band on a Bruker ER200D spectrometer at ambient temperature and at liquid-nitrogen temperature using a quartz-insertion Dewar. In all cases, the solvent used was a CH_2Cl_2–toluene mixture. Some of the niobium complexes had not been prepared before. They were prepared by the same method as related dithiophosphates, dithiocarbamates, and xanthates.[18,20] Spectra were simulated using a computer program based on that described by Evans *et al.*[23]

The complex $[V(\eta^5-C_5H_5)_2Cl_2]$ was obtained from Org-Met Inc., and used as received; $[Nb(\eta^5-C_5H_5)_2Cl_2]$ was prepared from $[Sn(n-C_4H_9)_3(C_5H_5)]$ and $NbCl_5$ as described by Bunker *et al.*[24] The vanadium dithiolate complexes were prepared in an analogous fashion, using a suspension of $[Nb(\eta^5-C_5H_5)_2Cl_2]$ in water (for dithiocarbamates and xanthates) or in the appropriate alcohol for the dithiophosphates. The anions PF_6^- or BF_4^- were used to precipitate the complexes.

Results and Discussion

The isotropic spectra of the vanadium complexes exhibited the expected eight lines (^{51}V; $I = \frac{7}{2}$) and of the niobium complexes the expected 10 lines (^{93}Nb; $I = \frac{9}{2}$). In the case of the dithiophosphates each of the eight vanadium lines was split by interaction of the unpaired electron with the ^{31}P ($I = \frac{1}{2}$) nucleus; because of greater linewidth the splitting in the niobium case was only observed for the five low-field lines. Likewise in the dithioarsenate complex further splitting to ^{75}As ($I = \frac{3}{2}$) was clearly resolved. The anisotropic spectra obtained from frozen solutions at liquid-nitrogen temperature showed two well resolved sets of hyperfine features; and a less well resolved third set whose g value and hyperfine coupling were calculated from $g_{iso} = \frac{1}{3}(g_x + g_y + g_z)$ and $A_{iso} = \frac{1}{3}(A_x + A_y + A_z)$. For both the niobium and vanadium compounds the g- and A-tensors are strongly anisotropic. On the other hand, for each complex the hyperfine coupling to phosphorus and arsenic is isotropic. All g values and metal hyperfine couplings were corrected for second-order effects. The corrected sets of parameters obtained are listed in Table 1, along with results from other workers for related complexes. Typical spectra are shown in Figure 1.

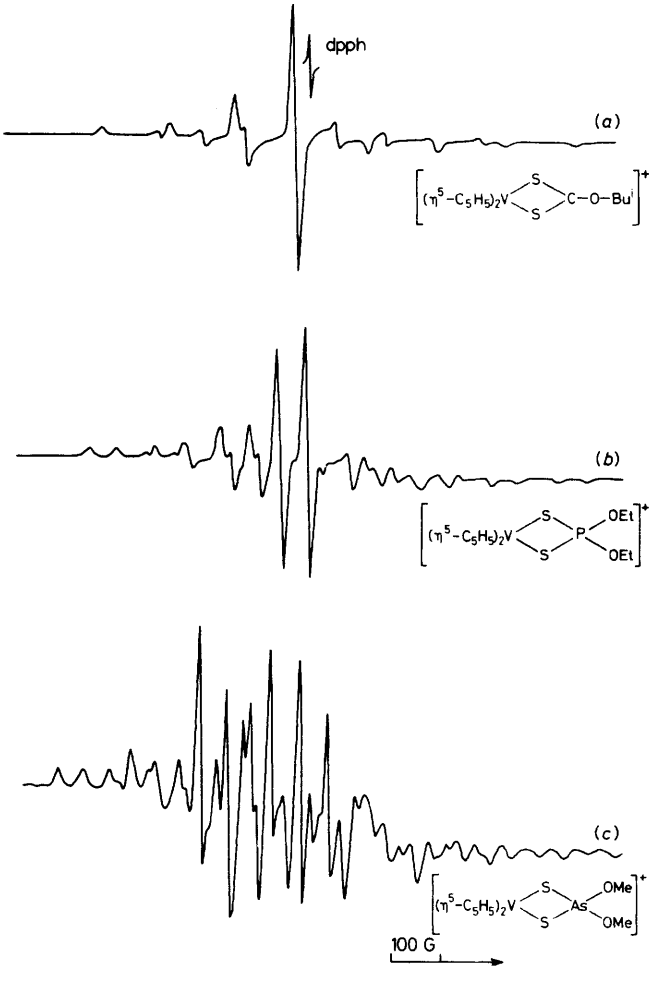


Figure 1. E.s.r. spectra of frozen solutions of $[V(\eta^5-C_5H_5)_2L_2]^+$ at 77 K (dpph = diphenylpicrylhydrazyl). (*a*) L_2 = isobutyl xanthate, (*b*) L_2 = diethyl dithiophosphate, and (*c*) L_2 = dimethyl dithioarsenate

Before the experimental hyperfine- and g-tensors can be analysed, the question of whether the principal axes of the

Table 1. E.s.r. parameters for complexes of the type $[M(\eta^5\text{-}C_5H_5)_2L_2]^{n+}$ (hyperfine couplings, $-\kappa P$ and P in units of cm^{-1})

Complex $[V(\eta^5\text{-}C_5H_5)_2L_2]^{n+}$		g_x	g_y	g_z	$-A_x$	$-A_y$	$-A_z$	a^2	b^2	a'^2	b'^2	κP	P	Ref.[a]
$L_2 = S_2CNR^1R^2$	$R^1 = H, R^2 = CH_3$	1.993	1.978	2.003	0.0068	0.0101	0.0014	0.96	0.04	0.43	0.57	0.0060	0.0086	
	$R^1 = R^2 = CH_3$	1.990	1.961	2.003	0.0070	0.0099	0.0014	0.97	0.03	0.40	0.60	0.0059	0.0083	
	$R^1 = R^2 = C_2H_5$	1.992	1.979	2.003	0.0068	0.0099	0.0014	0.97	0.03	0.42	0.58	0.0060	0.0085	
	$R^2 = R^2 = n\text{-}C_3H_7$	1.992	1.980	2.003	0.0067	0.0097	0.0014	0.97	0.03	0.42	0.58	0.0058	0.0083	
$L_2 = S_2COR$	$R = CH_3$	1.994	1.978	2.003	0.0068	0.0100	0.0014	0.97	0.03	0.42	0.58	0.0060	0.0085	
	$R = C_2H_5$	1.994	1.978	2.003	0.0068	0.0100	0.0014	0.97	0.03	0.43	0.57	0.0060	0.0085	
	$R = n\text{-}C_3H_7$	1.994	1.979	2.003	0.0068	0.0100	0.0014	0.97	0.03	0.42	0.58	0.0060	0.0085	
	$R = i\text{-}C_3H_7$	1.997	1.981	2.003	0.0068	0.0100	0.0014	0.97	0.03	0.42	0.58	0.0060	0.0085	
	$R = n\text{-}C_4H_9$	1.993	1.978	2.003	0.0068	0.0100	0.0014	0.97	0.03	0.42	0.58	0.0060	0.0085	
	$R = C_6H_{11}$	1.993	1.979	2.003	0.0068	0.0099	0.0014	0.97	0.03	0.42	0.58	0.0059	0.0085	
$L_2 = S_2C{=}CR^1R^2$	$R^1 = R^2 = CO(OMe)$	1.994	1.985	2.003	0.0068	0.0096	0.0014	0.97	0.03	0.41	0.59	0.0059	0.0083	
	$R^1 = R^2 = CO(OEt)$	1.992	1.986	2.003	0.0068	0.0097	0.0014	0.97	0.03	0.41	0.59	0.0059	0.0083	
	$R^1 = CO(OEt), R^2 = CN$	1.996	1.984	2.003	0.0068	0.0099	0.0014	0.97	0.03	0.42	0.58	0.0060	0.0085	
	$R^1 = R^2 = CN$	1.993	1.978	2.003	0.0068	0.0101	0.0014	0.96	0.04	0.43	0.57	0.0060	0.0086	
L_2 = mnt[b]		1.993	1.982	2.003	0.0065	0.0097	0.0014	0.96	0.04	0.44	0.56	0.0058	0.0083	
L_2 = dtpd[c]		1.992	1.989	2.003	0.0061	0.0094	0.0014	0.96	0.04	0.45	0.55	0.0056	0.0080	
$L_2 = S_2C{=}N{-}CN$		1.991	1.983	2.003	0.0069	0.0100	0.0014	0.97	0.03	0.42	0.58	0.0060	0.0086	
$L_2 = S_2P(OR)$	$R = CH_3$	1.993	1.973	1.998	0.0070	0.0104	0.0012	0.97	0.03	0.42	0.58	0.0061	0.0091	
	$R = C_2H_5$	1.992	1.973	2.002	0.0070	0.0104	0.0012	0.97	0.03	0.42	0.58	0.0061	0.0092	
$L_2 = S_2As(OCH_3)_2$		1.994	1.957	2.001	0.0068	0.0111	0.0014	0.95	0.05	0.46	0.54	0.0062	0.0094	
L_2 = acac[d]		1.982	1.957	1.998	0.0081	0.0113	0.0015	0.97	0.03	0.40	0.60	0.0067	0.0096	
L_2 = tfpd[e]		1.990	1.958	1.988	0.0081	0.0114	0.0015	0.97	0.03	0.41	0.59	0.0068	0.0100	
L_2 = hfpd[f]		1.987	1.950	1.997	0.0080	0.0114	0.0016	0.97	0.03	0.40	0.60	0.0068	0.0096	
L_2 = sal[g]		1.982	1.953	2.002	0.0081	0.0113	0.0014	0.98	0.02	0.39	0.61	0.0067	0.0097	
L_2 = hoqu[h]		1.986	1.964	2.002	0.0076	0.0105	0.0011	0.98	0.02	0.39	0.61	0.0062	0.0093	
L = NCO		1.987	1.955	1.995	0.0076	0.0121	0.0017	0.95	0.05	0.46	0.54	0.0069	0.0101	
L = NCO		1.985	1.957	2.000	0.0073	0.0119	0.0019	0.95	0.05	0.47	0.53	0.0068	0.0097	2
L = NCS		1.991	1.956	1.993	0.0073	0.0117	0.0018	0.95	0.05	0.46	0.54	0.0067	0.0097	

Table 1 (*continued*)

Complex $[V(\eta^5\text{-}C_5H_5)_2L_2]^{n+}$		g_x	g_y	g_z	$-A_x$	$-A_y$	$-A_z$	a^2	b^2	a'^2	b'^2	κP	P	Ref.[a]
L = NCS		1.988	1.958	2.000	0.0071	0.0115	0.0019	0.95	0.05	0.47	0.53	0.0067	0.0093	2
L = Cl	in toluene	1.986	1.971	2.010	0.0074	0.0118	0.0017	0.95	0.05	0.46	0.54	0.0068	0.0098	
	in toluene–acetone	1.986	1.974	2.007	0.0073	0.0118	0.0017	0.95	0.05	0.47	0.53	0.0068	0.0098	
	in thf–toluene [i]	1.984	1.974	2.009	0.0074	0.0118	0.0014	0.95	0.05	0.46	0.54	0.0067	0.0101	
	in CH_3CN–toluene	1.987	1.976	1.998	0.0073	0.0118	0.0022	0.94	0.06	0.48	0.52	0.0070	0.0094	
	in dmf [j]	1.987	1.973	1.974	0.0075	0.0117	0.0016	0.95	0.05	0.46	0.54	0.0067	0.0104	
	in CH_2Cl_2–toluene	1.986	1.970	2.011	0.0075	0.0118	0.0015	0.96	0.04	0.45	0.55	0.0068	0.0099	
	in CH_2Cl_2–toluene	1.986	1.971	2.000	0.0073	0.0115	0.0015	0.95	0.05	0.45	0.55	0.0066	0.0098	8
	in CH_2Cl_2–toluene	1.986	1.971	2.000	0.0074	0.0117	0.0015	0.95	0.05	0.46	0.54	0.0067	0.0100	2
	in CH_2Cl_2–toluene	1.965	1.946	1.967	0.0075	0.0119	0.0027	0.93	0.07	0.50	0.50	0.0070	0.0092	16
L = CN		1.994	1.986	2.000	0.0059	0.0099	0.0011	0.94	0.06	0.48	0.52	0.0055	0.0088	2
L = C_2H_5		1.977	2.000	1.993	0.0062	0.0101	0.0013	0.94	0.06	0.48	0.52	0.0057	0.0089	8
L = $CH_2Si(CH_3)_3$		1.997	1.999	1.999	0.0062	0.0107	0.0011	0.94	0.06	0.49	0.51	0.0059	0.0097	8
L_2 = S_5		1.996	2.000	1.969	0.0062	0.0104	0.0022	0.93	0.07	0.51	0.49	0.0061	0.0087	6
L_2 = $(=C{-}CO_2CH_3)_2$		2.001	1.982	2.002	0.0055	0.0071	0.0002	0.99	0.01	0.35	0.65	0.0042	0.0072	22
L_2 = $(=CH{-}CF_3)_2$		2.009	1.981	2.002	0.0059	0.0072	0.0002	0.99	0.01	0.32	0.68	0.0044	0.0074	22
L_2 = $(=N{-}C_6H_5)_2$		2.006	1.982	2.002	0.0061	0.0072	0.0002	1.00	0.00	0.31	0.69	0.0045	0.0075	22
Complex $[Nb(\eta^5\text{-}C_5H_5)_2L_2]^{n+}$														
L_2 = S_2CNR_2	R = CH_3	1.996	1.974	1.991	0.0081	0.0125	0.0034	0.94	0.06	0.49	0.51	0.0078	0.0090	
	R = C_2H_5	1.995	1.978	1.991	0.0081	0.0125	0.0034	0.94	0.06	0.49	0.51	0.0079	0.0091	
L_2 = S_2COR	R = CH_3	1.995	1.975	1.991	0.0081	0.0125	0.0034	0.94	0.06	0.49	0.51	0.0079	0.0090	
	R = C_2H_5	1.996	1.977	1.991	0.0081	0.0125	0.0034	0.94	0.06	0.49	0.51	0.0079	0.0091	
L_2 = $S_2P(OR)_2$	R = CH_3	1.996	1.954	1.990	0.0085	0.0129	0.0036	0.94	0.06	0.48	0.52	0.0081	0.0092	
	R = C_2H_5	1.995	1.954	1.991	0.0085	0.0129	0.0036	0.94	0.06	0.48	0.52	0.0081	0.0090	
	R = C_2H_5	2.001	1.963	1.999	0.0079	0.0123	0.0048	0.91	0.09	0.54	0.46	0.0082	0.0073	20
	R = i-C_4H_9	2.000	1.962	1.999	0.0078	0.0124	0.0047	0.91	0.09	0.55	0.45	0.0082	0.0075	20
L = Cl		2.003	1.945	1.983	0.0115	0.0162	0.0052	0.96	0.04	0.45	0.55	0.0107	0.0109	
L = Cl		1.980	1.940	2.000	0.0107	0.0160	0.0053	0.94	0.06	0.50	0.50	0.0103	0.0101	2
L = Cl copolymer attached		1.980	1.940	2.000	0.0107	0.0160	0.0053	0.94	0.06	0.50	0.50	0.0103	0.0101	1
L = NCS		1.987	1.935	2.000	0.0101	0.0154	0.0053	0.93	0.07	0.51	0.49	0.0100	0.0095	2
L = σ-C_5H_5		1.982	1.979	1.999	0.0091	0.0143	0.0044	0.92	0.08	0.52	0.48	0.0091	0.0098	2
L = CN		1.997	1.976	2.003	0.0077	0.0129	0.0053	0.87	0.13	0.61	0.39	0.0086	0.0076	2
$[Ta(\eta^5\text{-}C_5H_5)_2Cl_2]$		1.983	1.939	1.985	0.0071	0.0182	0.0070	0.75	0.25	0.75	0.25	0.0104	0.0124	11
$[Ta(\eta^5\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)_2]$		1.991	1.946	1.993	0.0062	0.0171	0.0061	0.75	0.25	0.75	0.25	0.0095	0.0121	19
$[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]^-$		1.982	1.959	2.002	0.0013	0.0019	0.0005	0.95	0.05	0.46	0.54	0.0012	0.0014	21

[a] This work unless otherwise stated. [b] mnt = Maleonitriledithiolate. [c] dtpd = Dithiopentane-2,4-dionate. [d] acac = Acetylacetonate. [e] tfpd = 1,1,1-Trifluoropentane-2,4-dionate. [f] hfpd = 1,1,1,5,5,5-Hexafluoropentane-2,4-dionate. [g] sal = Salicylaldehydate. [h] hoqu = 8-Hydroxyquinoline. [i] thf = Tetrahydrofuran. [j] dmf = Dimethylformamide.

hyperfine- and g-tensors are coincident must be answered. This can only be resolved unambiguously from e.s.r. single-crystal studies on systems where the structure of the isomorphous host has been determined. Full studies have only been carried out on $[V(\eta^5\text{-}C_5H_5)_2S_5]$ and $[V(\eta^5\text{-}C_5H_4CH_3)Cl_2]$.[6] In $[V(\eta^5\text{-}C_5H_5)_2S_5]$,[6] the g- and A-tensors were not coincident but in $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$ they were coincident. Furthermore, the directions of the A tensors of each were identical, being directed along (x) the line bisecting the Cl–V–Cl or S–V–S atoms, (y) perpendicular to the Cl–V–Cl or S–V–S plane, and (z) perpendicular to the plane bisecting the Cl–V–Cl or S–V–S atoms.[6] The non-coincident nature of the g- and A-tensors in $[V(\eta^5\text{-}C_5H_5)_2S_5]$ arises because of the lower symmetry compared with $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$ (the C_5H_5 rings are not equivalent and the VS_5 ring is chair-shaped). The coincidence of the A tensors for both molecules supports the notion that the directions of the metal hyperfine tensors are dependent only upon the *unpaired* electron distribution and independent of the type of ligand. In contrast, the g tensor reflects a changing electron magnetic moment due to changing orbital angular momentum which in turn is determined by the surrounding *overall* electrical charge distribution. Thus the inequivalence of the two C_5H_5 rings and different bonding between V and Cl and between V and S_5 causes the g tensors to be differently directed in $[V(\eta^5\text{-}C_5H_5)_2S_5]$ and $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$.

Whether coincidence of the g- and A-tensor axes occurs or not can be determined from powder spectra by simulation of the spectra.[25] Our spectra could be accurately simulated assuming coincident g- and A-axes whereas the relative intensities of some components of the spectra changed considerably when the x and y axes for the g-tensor were rotated relative to the A-tensor.

The spectral parameters were analysed using the equations derived from second-order perturbation theory by McGarvey[26] and presented in the following format [equations (1)—(6)] by Evans *et al.*[8]

$$A_x = -\kappa P + P[\alpha_x - (g_0 - g_x)] \tag{1}$$

$$A_y = -\kappa P + P[\alpha_y - (g_0 - g_y)] \tag{2}$$

$$A_z = -\kappa P + P[\alpha_z - (g_0 - g_z)] \tag{3}$$

$$\alpha_x = \frac{-2}{7}(a^2 - b^2) - \frac{4 \times 3^{\frac{1}{2}}ab}{7}\left[1 - \frac{(g_0 - g_z)}{8b^2}\right] - \frac{3^{\frac{1}{2}}}{14}\frac{(a + b \times 3^{\frac{1}{2}})(g_0 - g_y)}{(a \times 3^{\frac{1}{2}} - b)} \tag{4}$$

$$\alpha_y = \frac{-2}{7}(a^2 - b^2) + \frac{4 \times 3^{\frac{1}{2}}ab}{7}\left[\frac{1 - (g_0 - g_z)}{8b^2}\right] - \frac{3^{\frac{1}{2}}}{14}\frac{(a - b \times 3^{\frac{1}{2}})(g_0 - g_x)}{(a \times 3^{\frac{1}{2}} + b)} \tag{5}$$

$$\alpha_z = \frac{4}{7}(a^2 - b^2) + \frac{3^{\frac{1}{2}}}{14}\left[\frac{(a + b \times 3^{\frac{1}{2}})(g_0 - g_y)}{(a \times 3^{\frac{1}{2}} - b)} + \frac{(a - b \times 3^{\frac{1}{2}})(g_0 - g_x)}{(a \times 3^{\frac{1}{2}} + b)}\right] \tag{6}$$

Equations (1)—(6) assume that the unpaired electron is in the same type of orbital as found by Petersen and Dahl[6] for $[V(\eta^5\text{-}C_5H_5)_2Cl_2]$, *viz.* an orbital of A_1 symmetry in which the metal contribution has the form (7), where $a^2 + b^2 = 1$. Thus from these seven equations, the best values of a, b, P, and κ can be deduced. The hyperfine parameter $P = g_0 g_n \gamma_e \gamma_n \langle r^{-3} \rangle$ which gives direct information about electron delocalisation and covalency, and the spin-polarisation parameter κ relates $A_{\text{iso}} = -\kappa P + (g_{\text{iso}} - g_e)P$. The deduced values of a^2, b^2, P, and κ are given in Table 1.

$$|\psi_0\rangle = a|d_{z^2}\rangle + b|d_{x^2-y^2}\rangle \tag{7}$$

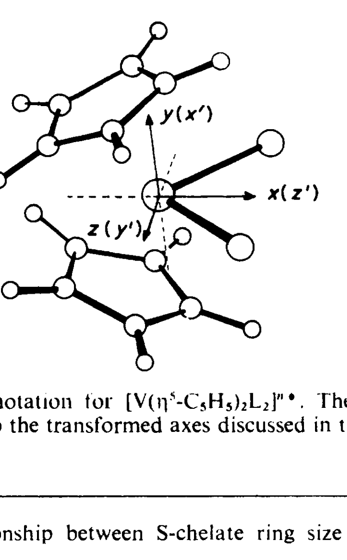


Figure 2. Axis notation for $[V(\eta^5\text{-}C_5H_5)_2L_2]^{n+}$. The notation in brackets refers to the transformed axes discussed in the text

Table 2. Relationship between S-chelate ring size and spin on vanadium, P

Ring size	$10^4P/\text{cm}^{-1}$
Planar 6	80
Planar 5	83
Planar 4	83–86
Non-chelate	88–100

From the deduced values of a^2, b^2, and P, we can conclude that the unpaired electron is largely in a d_{z^2} orbital in the axis scheme shown in Figure 2 as defined for the A-tensor by Petersen and Dahl.[6] However, since the C_2 symmetry axis bisects the Cl–V–Cl bond, then it may be more logical to define this as the z-axis. It is thus necessary to compute new values for a and b appropriate for an axis system transformed by simple permutation of the axis labels. If x becomes z', y becomes x', and z becomes y', then the coefficients a' and b' for the new $d_{z'^2}$ and $d_{x'^2-y'^2}$ orbitals respectively are $a' = -0.5a + 0.866b$ and $b' = -0.866a - 0.5b$.

For all the vanadium complexes, a'^2 ranges from 0.31 to 0.51 and b'^2 from 0.69 to 0.49, *i.e.* an almost equal amount of $d_{z'^2}$ and $d_{x'^2-y'^2}$ but with $d_{x'^2-y'^2}$ predominating. The values of P are in the range (80—100) × 10^{-4} cm^{-1} and may be compared with the P value, calculated from Clementi wavefunctions for a V^{4+} ion,[27] of 172 × 10^{-4} cm^{-1}. These show that the unpaired electron is *ca.* 46—58% localised on the metal. Closer inspection both of our results and those of others[2,6,8,16] shows that there is a good correlation between P and both the size of the chelating organic ring and the nature of the co-ordinating atom. Thus for sulphur co-ordinating atoms, the larger the ring size, the smaller is the value of P. This is summarised in Table 2. The decrease in P is associated with an increase in S–V–S bond angle (larger ring size) and is as expected since greater overlap between the V d_{z^2} orbital and the p_π orbital of the S, accompanied by greater delocalisation of the unpaired electron, is achieved when the S–V–S bond angle is larger. This is satisfying confirmation of the theoretical prediction by Lauher and Hoffmann.[28] The S–V–S bond angle in $[V(\eta^5\text{-}C_5H_5)_2S_5]$ is 89.3°, and cannot be compared with planar six-membered rings having larger angles because the VS_5 ring is puckered.[29] The larger value of P for $[V(\eta^5\text{-}C_5H_5)_2(\text{acac})]$-

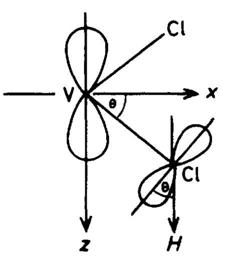
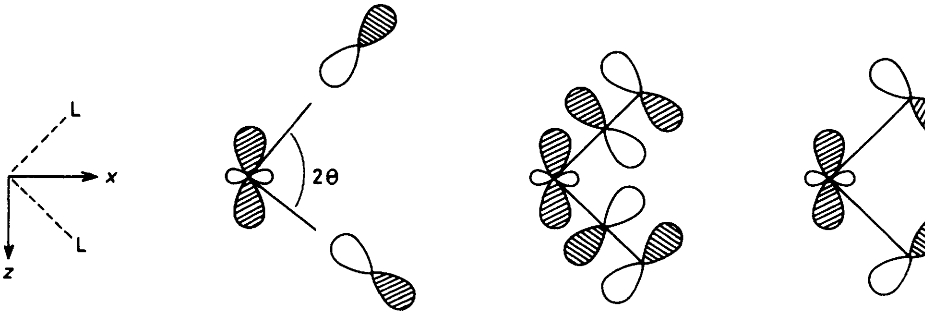


Figure 3. π-Bonding between a V d_{z^2} orbital and Cl π orbitals. The Cl–V–Cl angle, 2θ, is 87.1° in [$V(\eta^5-C_5H_4Me)_2Cl_2$]



σ π (acceptor) π (donor)

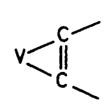
Figure 4. Orbitals involved in the VL_2 fragment of [$V(\eta^5-C_5H_5)_2L_2$]$^{n+}$

BF_4 (acac = acetylacetonate) compared with the thio-derivative, 96 × 10^{-4} and 80 × 10^{-4} cm^{-1} respectively, implies less delocalisation of the unpaired electron onto smaller p_π orbitals on oxygen. The complexes with non-chelating ligands and those chelates bonding *via* O or N all have larger *P* values, ranging from 88 × 10^{-4} to 100 × 10^{-4} cm^{-1}. Since they mostly involve smaller and more ionic atoms, then less delocalisation is expected.

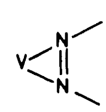
The absence of ligand hyperfine coupling in [$V(\eta^5-C_5H_5)_2Cl_2$], at least, is at first surprising since about 40% of the unpaired electron is delocalised onto the ligands. Since most of this unpaired electron is capable of interacting with a p_π orbital on each chlorine, then we have calculated what the expected hyperfine coupling to Cl might be. Taking the case of [$V(\eta^5-C_5H_4Me)_2Cl_2$] in particular, the Cl–V–Cl bond angle, 2θ, is 87.1°. When the applied magnetic field is along the *z* axis, the component of the dipolar coupling in the *z* direction to the Cl atom may be calculated by reference to Figure 3. If 20% of the electron is in the p_π orbital on each ^{35}Cl, then the expected anisotropic hyperfine coupling will be $0.2 \times 102 \times (3\cos^2\theta < 1) = 11.7$ G (1 G = 10^{-4} T), where a value 102 G is the expected anisotropic hyperfine coupling for an electron entirely in a ^{35}Cl *p* orbital. Since the linewidths of the narrowest parallel and narrowest isotropic features are only 10 and 6 G respectively, it suggests that delocalisation onto chlorine is less and that there is more delocalisation onto the C_5H_5 rings. We are currently investigating the ENDOR spectra of [$V(\eta^5-C_5H_5)_2Cl_2$] in frozen solution and find that there are sufficiently large proton couplings which, if they arise from spin-polarisation mechanisms, would imply significant spin density on the ring carbon atoms. The niobium complexes in general behave in a very similar manner: b^2 is slightly larger (from *ca.* 4 to 6%) which shows more dramatically in values of a'^2 and b'^2 which are more equal and with a'^2 sometimes the larger. Spin densities on the metal are almost the same for the vanadium and the niobium complexes (using $P = ca.\ 200 \times 10^{-4}$ cm^{-1} estimated for the Nb^{4+} ion). The two reported tantalum complexes, [$Ta(\eta^5-C_5H_5)_2Cl_2$][11] and [$Ta(\eta^5-C_5H_5)_2(\sigma-C_5H_5)_2$][19] are quite different. They both have $a^2 = 0.75$ and an estimated spin density on the metal of *ca.* 73%. The large increase may reflect a larger size and less efficient overlap with the Cl atoms.

The species [$Ti(\eta^5-C_5H_5)_2Cl_2$]$^-$ has been postulated[21] in irradiated [$Ti(\eta^5-C_5H_5)_2Cl_2$] and has a spin density on Ti of *ca.* 55% compared with 57.5% for the spin density on V in [$V(\eta^5-C_5H_5)_2Cl_2$]. The smaller value for Ti arises because of the orbital expansion due to the negative charge and consequent greater delocalisation of the electron. Extended Hückel calculations by Lauher and Hoffmann[28] on [$M(\eta^5-C_5H_5)_2L_2$] systems have shown that for σ-donor ligands the composition and energy of the non-bonding a_1 orbital is quite sensitive to the ligand interbond angle L–V–L (2θ) and that the angle 2θ decreases as *d* electrons are added to the metal. In our complexes, there is a π contribution to be considered from L. Two possibilities exist. If L is a π-acceptor, the ligand π* orbital is empty and there will be more delocalisation of the electron from the metal a_1 orbital as the angle 2θ increases (Figure 4). On the other hand, if L is a π-donor, the ligand π orbital is full and there is no delocalisation from the metal to ligand orbital, indeed they will be out of phase. It follows then that the metal a^1 electrons will be more localised on a_1 as 2θ increases.

The relative contributions *a* and *b* to the V a_1 (d_{z^2} and $d_{x^2-y^2}$) orbital vary as the type of ligand varies; *a* is found to be larger with those ligands L which are π-acceptors. This is consistent with the increased overlap of the ligand π-acceptor orbital with the d_{z^2} orbital, thus stabilising it (Figure 4). This is more dramatically seen in the complexes with the (*a*) and (*b*) groupings shown below, where there is considerable back bonding from the π-donor orbitals to the vanadium and corresponding low values of *P*.[22]



(*a*)



(*b*)

Acknowledgements

We thank the S.E.R.C. for a grant for equipment and the University of Melbourne for the opportunity of study leave (to A. T. C.).

References

1 N. H. Kilner and C. H. Brubaker, *Inorg. Chem.*, 1979, **18**, 3283.

2 C. P. Stewart and A. L. Porte, *J. Chem. Soc., Dalton Trans.*, 1973, 722.

3 I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Manzer, G. W. Parshall, and F. N. Tebbe, *J. Am. Chem. Soc.*, 1974, **96**, 7374; I. H. Elson and J. K. Kochi, *ibid.*, 1975, **97**, 1263.

4 H. H. Brintzineger, *J. Am. Chem. Soc.*, 1967, **89**, 6871.

5 J. G. Kenworthy, J. Myatt, and P. F. Todd, *J. Chem. Soc. B*, 1970, 791.

6 J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, 1975, **97**, 6416, 6422; E. G. Muller, S. F. Watkins, and L. F. Dahl, *J. Organomet. Chem.*, 1979, **111**, 73; E. G. Muller, J. L. Petersen, and L. F. Dahl, *J. Organomet. Chem.*, 1979, **111**, 91.

7 A. G. Evans, J. C. Evans, and E. H. Moon, *J. Chem. Soc., Dalton Trans.*, 1974, 2390.

8 A. G. Evans, J. C. Evans, D. J. C. Espley, P. H. Morgan, and J. Mortimer, *J. Chem. Soc., Dalton Trans.*, 1978, 57.

9 E. Samuel, G. Labauze, and D. Vivien, *J. Chem. Soc., Dalton Trans.*, 1979, 956.

10 G. Labauze, J. B. Raynor, and E. Samuel, *J. Chem. Soc., Dalton Trans.*, 1980, 2425.

11 A. H. Al-Mowali and W. A. A. Kuder, *J. Mol. Struct.*, 1979, **57**, 141.

12 A. H. Al-Mowali and W. A. A. Kuder, *J. Organomet. Chem.*, 1980, **194**, 61.

13 J. C. W. Chien and C. R. Bass, *J. Am. Chem. Soc.*, 1961, **83**, 3767.

14 G. Doyle and R. S. Tobias, *Inorg. Chem.*, 1968, **7**, 2479, 2484.

15 L. E. Manzer, *Inorg. Chem.*, 1977, **16**, 525; P. B. Hitchcock, M. F. Lappert, and C. R. C. Milne, *J. Chem. Soc., Dalton Trans.*, 1981, 180.

16 D. P. Bakalik and R. G. Hayes, *Inorg. Chem.*, 1972, **11**, 1734.

17 A. G. Evans, J. C. Evans, and J. Mortimer, *J. Am. Chem. Soc.*, 1979, **101**, 3204.

18 A. T. Casey and J. R. Thackeray, *Aust. J. Chem.*, 1972, **25**, 2085; 1974, **27**, 757; 1975, **28**, 471.

19 A. H. Al-Mowali, *J. Chem. Soc., Dalton Trans.*, 1980, 426.

20 C. Sanchez, D. Vivien, J. Livage, J. Sala-Pala, B. Viard, and J. E. Guerchais, *J. Chem. Soc., Dalton Trans.*, 1981, 64; B. Viard, J. Sala-Pala, J. Amaudrut, J. E. Guerchais, C. Sanchez, and J. Livage, *Inorg. Chim. Acta*, 1980, **39**, 99.

21 M. C. R. Symons and S. P. Mishra, *J. Chem. Soc., Dalton Trans.*, 1981, 2258.

22 J. L. Petersen and L. Griffith, *Inorg. Chem.*, 1980, **19**, 1852.

23 J. C. Evans, P. H. Morgan, and R. H. Renaud, *Anal. Chim. Acta*, 1978, **103**, 175.

24 M. J. Bunker, A. de Cean, and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1977, 59.

25 R. M. Golding and W. C. Tennant, *Mol. Phys.*, 1973, **25**, 1163.

26 B. R. McGarvey in ' Electron Spin Resonance of Metal Complexes,' ed. Teh Fu Yen, Plenum, New York, 1969.

27 B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135; *J. Inorg. Nucl. Chem.*, 1970, **32**, 3406.

28 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.

29 E. G. Muller, J. L. Petersen, and L. F. Dahl, *J. Organomet. Chem.*, 1976, **111**, 91.

Received 20*th December* 1982; *Paper* 2/2118