An Electron Paramagnetic Resonance Study of Tetracyclopentadienyltantalum(IV), [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$]

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X-Band e.s.r. spectra of magnetically dilute solutions of [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$] in $CHCl_3$ have been recorded at 77 and at 298 K and are analysed in detail. The spin-Hamiltonian parameters are listed, and are equated to the atomic orbital coefficients in the molecular orbitals involved in bonding. The unpaired electron lies essentially in the $5d_{x^2-y^2}$ metal-ion orbital and it is extensively delocalised on to the cyclopentadienide rings. The σ and π electrons of the cyclopentadienide rings are almost completely delocalised.

ELECTRON paramagnetic resonance studies of bis(η-cyclopentadienyl)-vanadium(IV) and -niobium(IV) complexes have previously been reported.[1-6] These include the complexes [V(η-C_5H_5)$_2X_2$] and [Nb(η-C_5H_5)$_2X_2$] (X = Cl, SCN, or OCN, for V; Cl, SCN, CN, or C_5H_5 for Nb), where in each case the unpaired electron lies essentially in the $n\ d_{z^2}$ orbital of the metal ion.

No e.s.r. studies have been reported for the analogous tantalum complexes. It was therefore decided to study the e.s.r. spectra obtained from magnetically dilute glasses which contain [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$] in order to obtain detailed quantitative information about the electronic distribution within this compound. The nature of the bonding is compared with that in the analogous vanadium and niobium complexes.

EXPERIMENTAL

Tetracyclopentadienyltantalum(IV), [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$], was prepared by allowing tantalum pentachloride to react with a suspension of sodium cyclopentadienide in benzene.[7]

E.s.r. spectra of thoroughly outgassed 10^{-3} mol dm^{-3} chloroform solutions of the complex were examined at 298 and 77 K in a Varian E-109 spectrometer. A typical spectrum recorded at 77 K is shown in the Figure. Electronic spectra were recorded in chloroform solution on a Pye-Unicam SP 8-100 spectrophotometer. The observed absorption maxima, $\nu_{max.}$/cm^{-1}, with absorption coefficients, ε/dm^3 mol^{-1} cm^{-1}, in parentheses are 14 000 (*ca.* 110), 16 000 (*ca.* 120), and 28 000 (*ca.* 1 200). The first and second of these are assigned to weak *d–d* transitions, the third to charge-transfer transitions.

TABLE 1

Spin-Hamiltonian parameters for metallocene complexes of vanadium(IV),[2] niobium(IV),[2] and tantalum(IV). Data refer to solutions in chloroform at 77 K, except for $\langle g \rangle$ and $\langle A \rangle$ which are the isotropic *g* factor and hyperfine coupling constant obtained from solution spectra at 298 K. All hyperfine tensor components are in units of cm^{-1}. Limits of error in the principal components of *g* and *A* are $\pm$0.000 7 and $\pm$0.000 08 cm^{-1} respectively

Compound	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}	$\langle g \rangle$	$\langle A \rangle$
[V(η-C_5H_5)$_2Cl_2$]	1.986 0	1.971 0	2.000 0	−0.007 40	−0.011 70	−0.001 52	1.993 4	−0.006 91
[Nb(η-C_5H_5)$_2Cl_2$]	1.980 0	1.940 0	2.000 0	−0.010 66	−0.015 98	−0.005 28	1.982 7	−0.010 68
[Nb(σ-C_5H_5)$_2$(η-C_5H_5)$_2$]	1.982 0	1.979 0	1.999 0	−0.009 08	−0.014 31	−0.004 37	1.988 0	−0.009 23
[Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$]	1.993 0	1.990 8	1.946 3	−0.006 05	−0.006 20	−0.017 08	1.976 5	−0.009 77

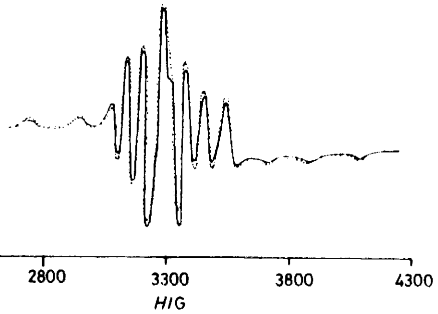
Analysis of E.P.R. Spectra.—It is assumed that [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$] has C_{2v} symmetry, and that the principal axes of the *g* tensor and the ^{181}Ta hyperfine interaction tensor, *A*, coincide. Since the analysis showed that the quadrupolar and Zeeman interactions at the tantalum nucleus are very weak in this compound, the spin Hamiltonian can therefore be written [8] in the diagonal form (1). The spin quantum number, *I*, is $\frac{7}{2}$ for ^{181}Ta(natural abundance = 100%) so the e.s.r. spectrum was analysed by

$$\mathcal{H} = \beta_e(g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_zS_z) + A_{xx}I_xS_x + A_{yy}I_yS_y + A_{zz}I_zS_z \quad (1)$$

fitting it [9,10] to curves of the form (2) where $S_{m_I}(H)$ is a Kneubühl function [11] and β is an appropriate Gaussian broadening factor. The spin-Hamiltonian parameters extracted from the spectrum shown in the Figure, together

$$F(H') = (2\pi)^{-\frac{1}{2}} \sum_{m_I = -7/2}^{+7/2} \int_{H=-\infty}^{+\infty} \beta^{-1} S_{m_I}(H) \exp[-(H'-H)^2(2\beta^2)^{-1}]dH \quad (2)$$

with the reported values [2] for analogous vanadium and niobium complexes, are listed in Table 1: analysis shows that the signs of A_{xx}, A_{yy}, and A_{zz} must all be identical. A spectrum computed from (2) using the data in Table 1 is also shown in the Figure.



Observed (——) and calculated (· · ·) e.s.r. spectra of a 10^{-3} mol dm^{-3} solution of [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$] in chloroform at 77 K

RESULTS AND DISCUSSION

Table 1 shows that the magnitudes of the principal values of the *g* and the hyperfine-tensor components in chloroform glasses can be used to distinguish between 'tetrahedral' species in which the unpaired electron lies essentially in the $d_{x^2-y^2}$ orbital and other 'tetrahedral' species in which the unpaired electron is known to be in the d_{z^2} orbital of the central metal ion.[1-6] The experimentally determined g and A tensors for $[Ta(\sigma\text{-}C_5H_5)_2(\eta\text{-}C_5H_5)_2]$ could only be accommodated by placing the unpaired electron in a molecular orbital of ψ^* (A_1) symmetry derived mainly from the $d_{x^2-y^2}$ orbital of the central metal ion. Furthermore, the very small deviation from axial symmetry in both the g and A tensors indicates that the contribution of the metal-ion d_{z^2} orbital to the ground state, ψ^* (A_1), containing the unpaired electron is very small.

TABLE 2

Molecular-orbital coefficients and metal-ion d-orbital populations for metallocene complexes of vanadium,[2] niobium,[2] and tantalum. χ in atomic units

Compound	k	χ	$\lvert a\rvert$	$\lvert b\rvert$	$(\alpha^*)^2$	$P_{md}(B_2^*)$	$P_{md}(B_1^*)$	$P_{md}(A_2^*)$
$[V(\eta\text{-}C_5H_5)_2Cl_2]$	0.64	−2.195	0.223	0.975	0.970	0.553	0.582	
$[Nb(\eta\text{-}C_5H_5)_2Cl_2]$	0.98	−3.68	0.274	0.963	1.000	0.456	0.520	
$[Nb(\sigma\text{-}C_5H_5)_2(\eta\text{-}C_5H_5)_2]$	0.85	−3.80	0.276	0.962	0.915	0.455	0.440	
$[Ta(\sigma\text{-}C_5H_5)_2(\eta\text{-}C_5H_5)_2]$	0.84	−7.30	0.998	0.002	0.840	0.414	0.428	0.400

More precise information can be obtained about electron distributions within this complex if the parameters of the spin Hamiltonian are equated with the coefficients of appropriate linear combinations of atomic orbitals. On the basis of ligand-field theory, in a C_{2v} complex, tantalum-ion orbitals combine with cyclopentadienyl-group orbitals with appropriate symmetry to form the magnetically important bonding and antibonding molecular orbitals for the complex [equations (3)—(9) where ϕ_{cp} are the cyclopentadienyl-group

$$\psi^*(A_1) = \alpha^*(ad_{x^2-y^2} + bd_{z^2}) + (\alpha^*)'\phi_{\sigma\text{-cp}} \qquad (3)$$

$$\psi(A_2) = \beta d_{xy} + \beta'\phi_{\pi\text{-cp}} \qquad (4)$$

$$\psi^*(A_2) = \beta^* d_{xy} + (\beta^*)'\phi_{\pi\text{-cp}} \qquad (5)$$

$$\psi(B_1) = \gamma d_{xz} + \gamma'\phi_{\sigma\text{-cp}} \qquad (6)$$

$$\psi^*(B_1) = \gamma^* d_{xz} + (\gamma^*)'\phi_{\sigma\text{-cp}} \qquad (7)$$

$$\psi(B_2) = \delta d_{yz} + \delta'\phi_{\pi\text{-cp}} \qquad (8)$$

$$\psi^*(B_2) = \delta^* d_{yz} + (\delta^*)'\phi_{\pi\text{-cp}} \qquad (9)$$

orbitals of appropriate symmetry].[2] If the matrix elements of the spin–orbit coupling at the tantalum ion, plus the true Zeeman and hyperfine interaction, are now equated to the corresponding matrix elements of the

$$g_{zz} = 2.002\,3 - 8a^2\alpha^{*2}\xi\left\{\frac{P_{md}(A_2^*)}{\Delta E(A_2^*)} - \frac{[1 - P_{md}(A_2^*)]}{\Delta E(A_2)}\right\} \qquad (10)$$

$$g_{xx} = 2.002\,3 - 2a[a + 2(3^{\frac{1}{2}}b)]\alpha^{*2}\xi\left\{\frac{P_{md}(B_2^*)}{\Delta E(B_2^*)} - \frac{[1 - P_{md}(B_2^*)]}{\Delta E(B_2)}\right\} \qquad (11)$$

spin Hamiltonian (1) then relationships (10)—(18) for the principal components of the g and A tensors may be deduced from standard perturbation theory.[2,12] Here ξ is the spin–orbit coupling constant of the tantalum ion, k is the isotropic contact term, χ is the spin polarisation, and $P_{md}(\psi)$ is the metal-ion d-orbital population in the molecular orbital, ψ. The terms $\Delta E(\psi)$ and $\Delta E(\psi^*)$ are the energies [relative to that of the $\psi^*(A_1)$ level] of the appropriate bonding and antibonding excited levels.

Bonding in $[Ta(\sigma\text{-}C_5H_5)_2(\eta\text{-}C_5H_5)_2]$.—In order to obtain the values of the bonding parameters from equations (10)—(15), estimates of the values of ξ and P for the tantalum ion together with the assignment of the band maxima in the electronic absorption spectrum were needed. The value of ξ was estimated[2,13] to be 1 100

$$g_{yy} = 2.002\,3 - 2a[a - 2(3^{\frac{1}{2}}b)]\alpha^{*2}\xi\left\{\frac{P_{md}(B_1^*)}{\Delta E(B_1^*)} - \frac{[1 - P_{md}(B_1^*)]}{\Delta E(B_1)}\right\} \qquad (12)$$

$$A_z = P\left\{-k - \frac{4}{7}a^2\alpha^{*2} - \frac{1}{14}\frac{[3a + (3^{\frac{1}{2}}b)]}{[a - (3^{\frac{1}{2}}b)]}(2.002\,3 - g_{yy}) - \frac{1}{14}\frac{[3a - (3^{\frac{1}{2}}b)]}{[a + (3^{\frac{1}{2}}b)]}(2.002\,3 - g_{xx}) - (2.002\,3 - g_{zz})\right\} \qquad (13)$$

$$A_{xx} = P\left\{-k + \frac{2}{7}a^2\alpha^{*2} - \frac{4}{7}(3)^{\frac{1}{2}}ab\alpha^{*2} - (2.002\,3 - g_{xx}) + \frac{1}{14}\frac{[3a + (3^{\frac{1}{2}}b)]}{[a - (3^{\frac{1}{2}}b)]}(2.002\,3 - g_{yy}) - \frac{1}{7}\frac{b}{a}(2.002\,3 - g_{zz})\right\} \qquad (14)$$

$$A_{yy} = P\left\{-k + \frac{2}{7}a^2\alpha^{*2} + \frac{4(3)^{\frac{1}{2}}}{7}ab\alpha^{*2} - (2.002\,3 - g_{yy}) + \frac{1}{14}\frac{[3a - (3^{\frac{1}{2}}b)]}{[a + (3^{\frac{1}{2}}b)]}(2.002\,3 - g_{xx}) + \frac{1}{7}\frac{b}{a}(2.002\,3 - g_{zz})\right\} \qquad (15)$$

$$\langle A\rangle = -Pk - (2.002\,3 - \langle g\rangle)P \qquad (16)$$

$$P = 2.002\,3g_n\beta_e\beta_n\langle r^{-3}\rangle \qquad (17)$$

$$k = -2.002\,3g_n\beta_e\beta_n\frac{2}{3}\chi \qquad (18)$$

cm^{-1}, after making allowance for charge and configuration as described in the molecular-orbital calculations carried out on $[V(\eta\text{-}C_5H_5)_2Cl_2]$.[2] A value of 0.011 44 cm^{-1} was obtained for P by applying equations (13)—(15) to the experimental hyperfine coupling tensors. The positions, intensities, and consistency with the e.s.r. data indicate that the band maxima in the electronic absorption band should be assigned to the transitions listed below.

Band maximum (cm^{-1})	Transition
14 000	$\psi^*(A_2)\leftarrow\psi^*(A_1)$
16 000	$\psi^*(B_1)\leftarrow\psi^*(A_1)$ $\psi^*(B_2)\leftarrow\psi^*(A_1)$
28 000	$\psi^*(A_1)\leftarrow\psi(B_1)$ $\psi^*(A_1)\leftarrow\psi(B_2)$ $\psi^*(A_1)\leftarrow\psi(A_2)$

The spin-Hamiltonian parameters, ξ, and P values together with the assignment of the band maxima now enable the values k, a, b, and α^* to be evaluated by using equations (10)—(15). The parameters obtained in this way for [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$] together with the reported values for [V(η-C_5H_5)$_2$$Cl_2$], [Nb($\eta$-$C_5H_5$)$_2$$Cl_2$], and [Nb($\sigma$-$C_5H_5$)$_2$($\eta$-$C_5H_5$)$_2$] are listed in Table 2. The metal-ion d-orbital populations in the $\psi^*(A_2)$, $\psi^*(B_1)$, and $\psi^*(B_2)$ molecular orbitals, $P_{\mathrm{md}}(A_2^*)$, $P_{\mathrm{md}}(B_1^*)$, and $P_{\mathrm{md}}(B_2^*)$, may then be estimated from equations (10)—(12). Calculated values of these populations are also listed in Table 2.

On the basis of calculated values of k and χ for [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$], it appears that the direct 6s tantalum contribution to the molecular orbital $\psi^*(A_1)$ must be sufficiently small so that the major contribution to χ arises mostly from the spin-polarisation mechanism. An increase in the negative value of χ for [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$] indicates that the amount of 6s tantalum-orbital character in $\psi^*(A_1)$ is smaller than the amount of 4s and 5s orbital characters in the corresponding vanadium and niobium complexes.

The magnitude of $(\alpha^*)^2$ in Table 2 for [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$] shows that the unpaired electron resides essentially on the tantalum orbitals, but it is partially (16%) delocalised on to the σ-bonded ligands. We were not able to resolve ligand hyperfine coupling in the e.s.r. spectra, but linewidth measurements are consistent with *ca.* 20% delocalisation on to the ligands. Little delocalisation of the unpaired electron is found in the analogous compounds of vanadium and niobium.

The calculated values of the mixing coefficients a and b for [Ta(σ-C_5H_5)$_2$(η-C_5H_5)$_2$] show that the unpaired electron is located in a molecular orbital composed primarily of the $d_{x^2-y^2}$ orbital mixed with a negligibly small amount of d_{z^2} orbital character. In the vanadium and niobium complexes, the values of a and b show that in each case the unpaired electron lies essentially in the metal-ion d_{z^2} orbital mixed with a small but significant amount of $d_{x^2-y^2}$ orbital. It therefore appears that there are significant differences in the structures of the vanadium, niobium, and tantalum complexes, the ligands in the tantalum complex being closer to the molecular Z axis, so that the Coulomb interaction between the tantalum and the ligand orbitals along this axis enhances the contribution of the $d_{x^2-y^2}$ orbital to the molecular orbital $\psi^*(A_1)$ containing the unpaired electron and lowers the contribution of the d_{z^2} orbital to $\psi^*(A_1)$.

The $P_{\mathrm{md}}(B_2^*)$ and $P_{\mathrm{md}}(B_1^*)$ values in Table 2, which reflect the extent of delocalisation of the π and σ electrons away from the ligands into the metal-ion d_{yz} and d_{xz} orbitals respectively, show that these electrons are completely delocalised and are shared almost equally between the ligands and the metal. These data also show that there is more delocalisation in the tantalum than in the vanadium and niobium complexes. The small difference between the $P_{\mathrm{md}}(B_2^*)$ and $P_{\mathrm{md}}(B_1^*)$ values for the tantalum complex exerts only a small influence on the $g_{\perp}$ anisotropy. Therefore it follows that the difference in the tensor components g_{xx} and g_{yy} is essentially due to the small contributions from the tantalum d_{z^2} orbital to the $\psi^*(A_1)$ orbital containing the unpaired electron.

The estimated value of $P_{\mathrm{md}}(A_2^*)$ for the tantalum complex, which reflects the degree of delocalisation of π electrons into the metal-ion d_{xy} orbital, also shows that these electrons are completely delocalised and are shared almost equally between the ligands and the metal ion. The electronic distribution in the $\psi^*(A_2)$ molecular orbitals of vanadium and niobium complexes cannot be described by use of g_{zz} since the unpaired electron is mainly localised in the d_{z^2} orbitals.

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REFERENCES

[1] D. P. Bakalik and R. G. Hayes, *Inorg. Chem.*, 1972, **11**, 1734.

[2] C. P. Stewart and A. L. Porte, *J.C.S. Dalton*, 1973, 722.

[3] A. G. Evans, J. C. Evans, and E. H. Moon, *J.C.S. Dalton*, 1974, 2390.

[4] J. L. Peterson and L. F. Dahl, *J. Amer. Chem. Soc.*, 1974, **96**, 2248.

[5] J. L. Peterson and L. F. Dahl, *J. Amer. Chem. Soc.*, 1975, **97**, 6416.

[6] J. L. Peterson and L. F. Dahl, *J. Amer. Chem. Soc.*, 1975, **97**, 6422.

[7] A. V. Baalen, C. J. Groenenboom, and H. J. Deliefde Meijer, *J. Organometallic Chem.*, 1974, **74**, 245.

[8] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.*, 1951, **A205**, 135.

[9] Ali H. Al-Mowali and A. L. Porte, *J.C.S. Dalton*, 1974, 366.

[10] Ali H. Al-Mowali and A. L. Porte, *J.C.S. Dalton*, 1975, 51.

[11] F. K. Kneubühl, *J. Chem. Phys.*, 1960, **33**, 1074.

[12] B. R. McGarvey, *Transition Metal Chem.*, 1966, **3**, 89 and refs. therein.

[13] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 235 and refs. therein.