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ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF DICYCLOOCTATETRAENYL-TITANIUM AND -VANADIUM COMPLEXES

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Summary

The symmetry and the nature of the molecular orbitals of dicyclooctatetraenyl-titanium and -vanadium complexes have been investigated by means of group theory. These results and the overlap integrals previously estimated by Fischer have allowed us to propose an electronic configuration for these complexes. This molecular orbital diagram is in agreement with magnetic susceptibility and EPR results obtained for the vanadium complex.

Introduction

Dicyclooctatetraenyl—metal complexes have received considerable attention because of their high symmetry. The electronic configuration and the bonding in this class of compounds have been the subject of some investigation, particularly for actinide complexes. Streitwieser et al. [1] have proposed an electronic structure for dicyclooctatetraenyl-thorium and -uranium compounds. Crystallographic studies [2] have shown that these two molecules have a "sandwich" structure, with planar eight-member C_8H_8 rings above and below the Th^{IV} or the U^{IV} ions in a D_{8h} molecular symmetry. The magnetic properties [3] as well as the electronic spectra and molecular orbital calculations [4] have been reported for a few actinide complexes.

The dicyclooctatetraenyltitanium compound [5] does not have such a high symmetry: the true molecular symmetry is very low (C_s). The molecule contains both a symmetrically bonded (local symmetry C_{8v}) and an asymmetrically bonded (local symmetry C_s) ring. Schwartz et al. [6] have studied the intramolecular ring "flipping" of this complex by NMR spectroscopy. It is reasonable to suppose that the V complex has the same structure and this is strongly supported by vibrational studies which have shown that the symmetric ring is more firmly bonded than the asymmetric one [7].

The purpose of this work is to study the nature and symmetry of the molecular orbitals for both Ti and V complexes, assuming a C_{8v} local symmetry. These orbitals will be slightly split by the presence of the weakly bound asymmetric ring. The resulting energy-level diagram is confirmed by experimental magnetic susceptibility and EPR spectra results.

Results

Magnetic susceptibility measurements

The dicyclooctatetraenyltitanium complex is known to be diamagnetic [6]. On the contrary, the V complex has a magnetic moment corresponding to one unpaired electron. Measurements over the range 4-293 K were made and the behaviour of the magnetic susceptibilities as a function of temperature is illustrated in Fig. 1.

The vanadium complex shows normal Curie temperature dependence: the magnetic moment calculated from the slope of the Curie plot is 1.5 B.M., indicating an important spin—orbit interaction [8].

EPR spectra results

The general features of our EPR spectra may be summarized as follows:

(a) In solution, a typical correlation spectrum of the vanadium ion is observed (Fig. 2); it shows eight lines of equal intensities in accordance with the nuclear spin $I = 7/2$ of ^{51}V. The spectrum indicates clearly that $g_{iso} = 1.9876$ and $A_{iso} = 81.1$ Oe.

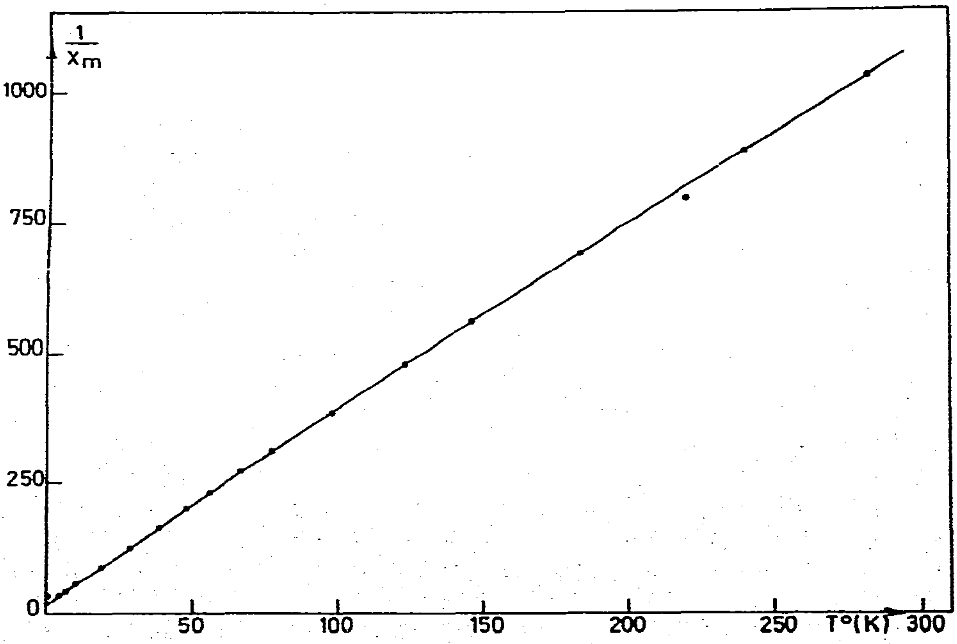

Fig. 1. Curie plot for the $(C_8H_8)_2V$ complex.

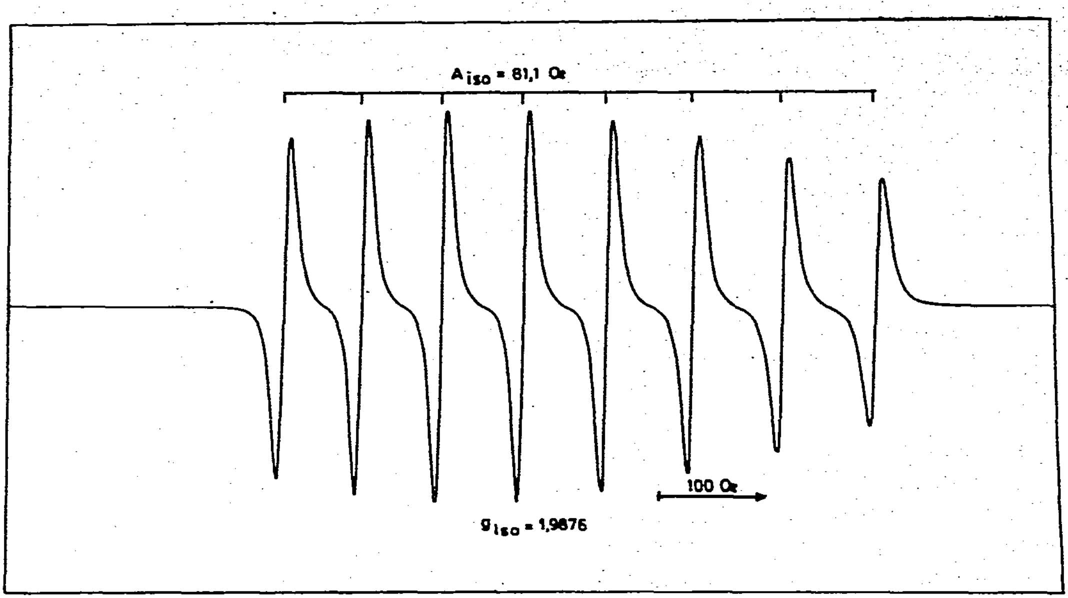

Fig. 2. EPR spectrum of $(C_8H_8)_2V$ in benzene solution at 293 K.

(b) The EPR spectrum of the solid or of the frozen solution consists of two main features: a strong asymmetrical line, the broader part of which extends towards high fields (Fig. 3), the peak-to-peak line width being 21 Oe; eight weak satellite lines (about 200 times less in intensity) due to an interaction with the ^{51}V

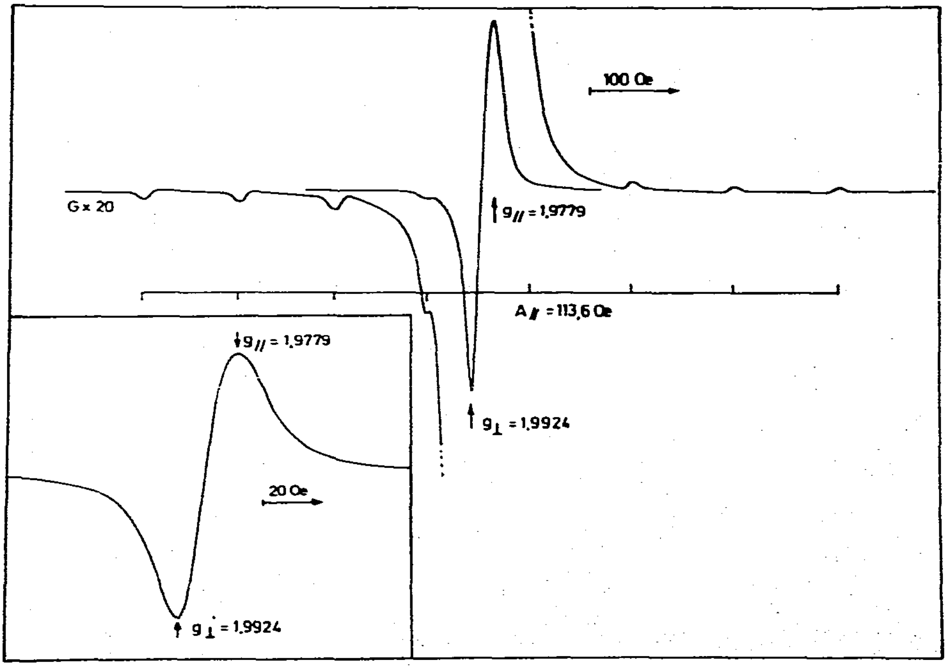

Fig. 3. EPR spectrum of a frozen solution of $(C_8H_8)_2V$ at 77 K.

TABLE 1

EPR PARAMETERS OF DICYCLOOCTATETRAENYLVANADIUM

	g-values [a]			A-values [b]		
	g_{iso}	$g_{\parallel}$	$g_{\perp}$	A_{iso}	$A_{\parallel}$	$A_{\perp}$
Solid	—	1.9789	1.9919	—	—	—
Solution						
(300 K)	1.9876	—	—	81.1	—	—
(77 K)	—	1.9779	(1.9924) [c]	—	113.6	(64.8) [d]

[a] All g-values in this work ±0.0007. [b] All A-values in Oersted units. [c] Calculated values: $g_{\perp} = \frac{1}{2}(3\,g_{iso} - g_{\parallel})$. [d] Calculated value: $A_{\perp} = \frac{1}{2}(3\,A_{iso} - A_{\parallel})$.

nucleus, the phase of which is positive on the high-field side of the main centre line and negative on the low-field side of the centre signal (Fig. 3).

The main centre line is attributed to V species in strong exchange interaction with each other for which the rate of exchange is much higher than the nuclear hyperfine splitting. These eight weak satellites are centred on the $g_{\parallel}$-value, as determined from the centre line shape; we assign them to the same species but with a much smaller exchange interaction. From these observations, we calculate $A_{\parallel}$ = 113.6 Oe, $g_{\perp}$ = 1.9924 and $g_{\parallel}$ = 1.9779. It is of interest to note that the g_{iso}-value corresponding to these EPR parameters is just that found in the fluid solution, hence confirming our assignment of the g-values.

Our assignment of the EPR spectra is given in Table 1 with calculated values in parentheses. These values are in contradiction with the original assignment of

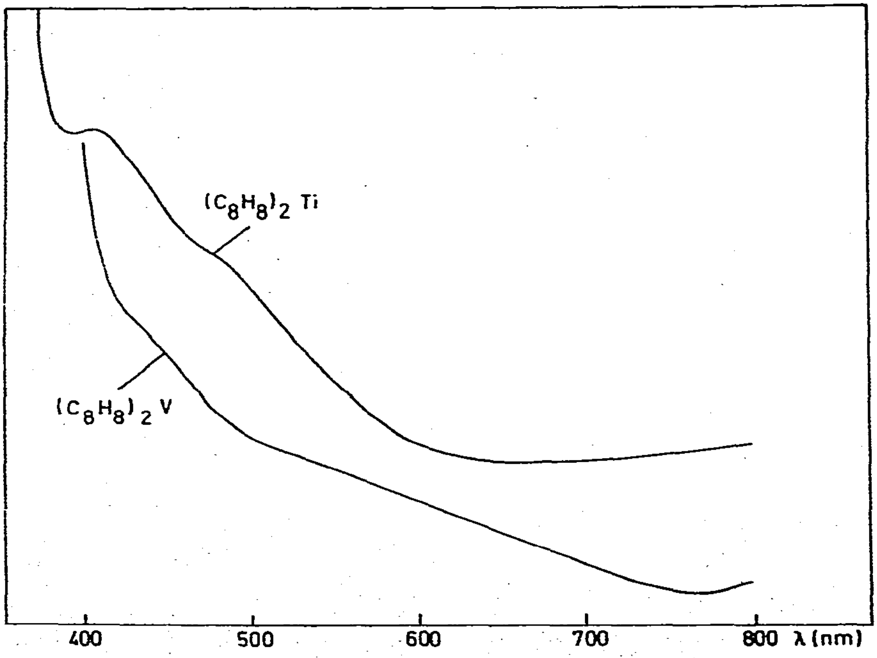

Fig. 4. Electronic spectra of $(C_8H_8)_2Ti$ and $(C_8H_8)_2V$.

Thomas and Hayes [9] but our results are confirmed by the same EPR parameters obtained for the complex prepared by two different methods (see experimental part).

Electronic spectra

The room-temperature electronic absorption spectra of the Ti and V complexes are presented in Fig. 4. The Ti compound shows two absorption bands at 405 and 490 nm, but the V complex has very weak absorption bands in the visible region.

Discussion

Molecular orbitals of the C_8H_8—M system

For a C_{8v} ligand field, the eight molecular orbitals of the C_8H_8 ring belong to a reducible representation giving rise to the following decomposition:

$$1A_1 + 1B_2 + 1E_1 + 1E_2 + 1E_3$$

By use of the projection operators, we have calculated the basic functions of these irreducible representations: the linear combinations of π-ring orbitals are given in Table 2. The relative energies of the C_8H_8 orbitals have been estimated by means of the Hückel method [10] and are also given in Table 2.

The character table of the C_{8v} group [11] includes the symmetry of atomic orbitals of the metal and the results are given in Table 3 together with Fischer's estimates of the energy of these orbitals [10].

The schematic energy-level diagram for the C_8H_8—M system is given in Fig. 5 where we have reported the approximate orbital energies of the ring and the metal. According to Fischer's estimates of ring—metal overlaps and of orbital energies in the C_8H_8—Ti system [10], the $a_1(d_{z^2})$ and $a_1(p_z)$ overlaps with the ring are small and the corresponding molecular orbitals are essentially non-bonded. In contrast, the overlap of other metal orbitals with corresponding π-ring orbitals are large and the resulting molecular orbitals of the complex are very important. Nevertheless, by examination of the relative ring and metal orbital energies, the $e_2(d_{x^2-y^2}, d_{xy})$ metal orbitals are more tightly bound to the orbitals of the ring

TABLE 2

π-RING C_8H_8 ORBITALS IN A C_{8v} SYMMETRY

Irreducible representation	Molecular orbitals	Energy (eV)
A_1	$8^{-1/2}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 + \phi_7 + \phi_8)$	—15
E_1	$8^{-1/2}(\sqrt{2}\phi_1 + \phi_2 - \phi_4 - \sqrt{2}\phi_5 - \phi_6 + \phi_8)$ $8^{-1/2}(\phi_1 + \sqrt{2}\phi_2 + \phi_3 - \phi_5 - \sqrt{2}\phi_6 - \phi_7)$	—13
E_2	$2^{-1}(\phi_1 - \phi_3 + \phi_5 - \phi_7)$ $2^{-1}(\phi_2 - \phi_4 + \phi_6 - \phi_8)$	—9
E_3	$8^{-1/2}(\sqrt{2}\phi_1 - \phi_2 + \phi_4 - \sqrt{2}\phi_5 + \phi_6 - \phi_8)$ $8^{-1/2}(-\phi_1 + \sqrt{2}\phi_2 - \phi_3 + \phi_5 - \sqrt{2}\phi_6 + \phi_7)$	—5
B_2	$8^{-1/2}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6 + \phi_7 - \phi_8)$	—3

TABLE 3

METAL ORBITALS IN A C_{8v} SYMMETRY

Atomic orbitals	Irreducible representation	Energy (eV)	
		Ti^0	V^0
s	A_1	—6.83	—6.76
p	$1A_1(p_z) + 1E_1(p_x,p_y)$	—7.48	—7.41
d	$1A_1(d_{z^2}) + 1E_1(d_{xz},d_{yz})$ $+ 1E_2(d_{x^2-y^2},d_{xy})$	—4.98	—4.91

than the $e_1(d_{xz},d_{yz}$ and $p_x,p_y)$ orbitals, although the latter have overlap integrals that are somewhat larger than the former. These considerations allow us to report only bonding molecular orbitals in the energetic order quoted in Fig. 5.

Electronic configurations

The electronic configurations of the Ti and V complexes are obtained by assignment of formal oxidation states for metals and ligands: +2 for the metal ion and —2 for the C_8H_8 aromatic ring, the C_8H_8—M system being a neutral group slightly bonded to an asymmetric neutral C_8H_8 ring. This is confirmed by the NMR spectra of the $(C_8H_8)_2Ti$ complex for which an intramolecular redox reaction occurs for the planar and bent C_8H_8 ligand rings, the two rings being bonded to a Ti(II) central ion [6].

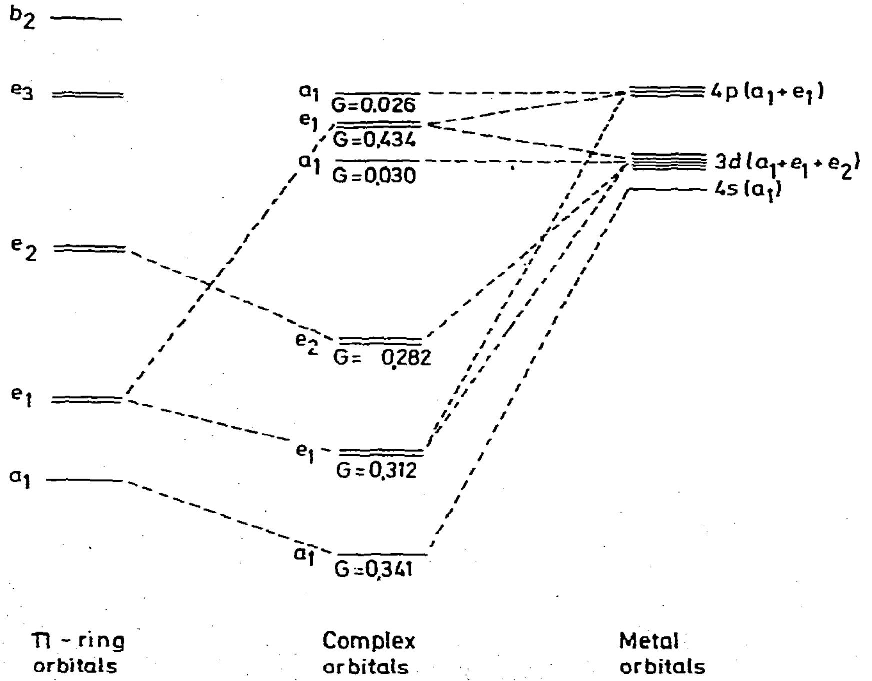

Fig. 5. Schematic energy-level diagram for the $(C_8H_8)M$ system assuming a C_{8v} symmetry. The G-values indicate the results of overlap integrals estimated by Fischer [10].

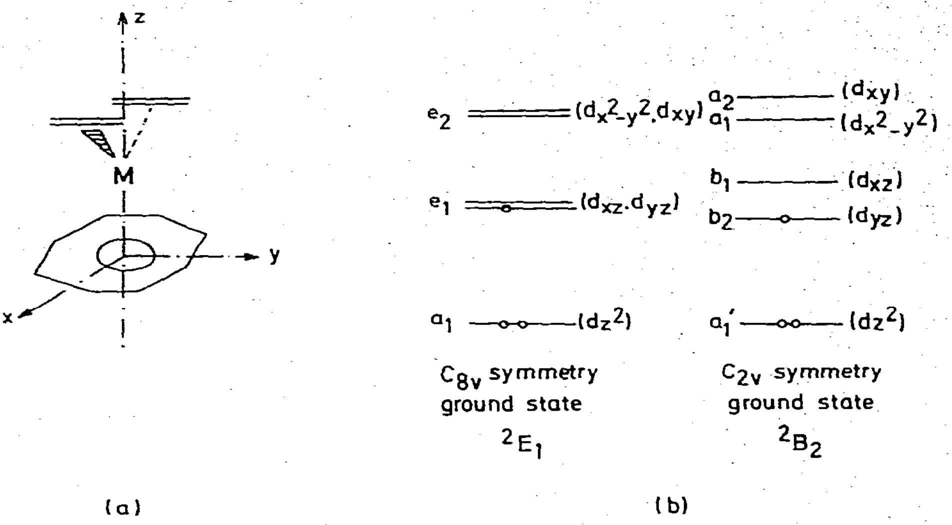

Fig. 6. Crystal field splittings of the *d*-orbitals for C_{8v} and C_{2v} symmetry.

The electronic configurations for the (C_8H_8)—M systems are therefore the following:

for the Ti complex $(a_1)^2(e_1)^4(e_2)^4(a_1)^2$
for the V complex $(a_1)^2(e_1)^4(e_2)^4(a_1)^2(e_1)^1$

This is in agreement with experimental magnetic susceptibility results: the Ti compound is diamagnetic and the V complex paramagnetic with one unpaired electron. Moreover, the *g*-factors estimated from EPR spectra ($g_\parallel < g_e$ and $g_\perp > g_\parallel$) show that the unpaired electron resides in an orbital which is not symmetrical along the *z*-axis.

From our schematic energy-level diagram, the only other possibility is that this unpaired electron resides in an e_1 orbital. The ground state of such a system is consequently a $^2E_1$ term which is slightly split by the presence of the weakly bound asymmetric ring. By assuming a global C_{2v} symmetry (Fig. 6a), this term is decomposed to $^2B_1 + {}^2B_2$ (the fundamental state is probably $^2B_2$ according to the coordinate system quoted in Fig. 6a). The resulting ligand field scheme is given in Fig. 6b, which shows only the splitting of the *d*-orbitals. Nevertheless, a more complete treatment does take account of the 3*d*—4*p* mixing and the function representing the ground state can thus be written as:

$$|b_2\rangle = c_1|d_{yz}\rangle + c_2|p_y\rangle$$

The relative amplitudes c_1 and c_2 are not easily estimated. A crystal-field splitting of the *d*-orbitals gives the following *g*-factors [12]:

$$g_{zz} = 2.0023 - \frac{2\lambda}{E(^2B_1) - E(^2B_2)}$$

$$g_{xx} = 2.0023 - \frac{2\lambda}{E(^2A_1) - E(^2B_2)} - \frac{6\lambda}{E(^2A_1') - E(^2B_2)}$$

$$g_{yy} = 2.0023 - \frac{2\lambda}{E(^2A_2) - E(^2B_2)}$$

where λ is the spin—orbit coupling constant ($\lambda = 170$ cm^{-1} for V^{II} in a ligand field giving $S = \frac{1}{2}$) [8] ${}^2B_1$, ${}^2A_1$, and ${}^2A_2$ are excited states of the complex, and ${}^2A_1'$ a spin-paired level.

The C_{2v} splitting is probably weak as we observe from EPR spectra which shows a typical axial symmetry ($g_\parallel = g_{zz} = 1.9779$ and $g_\perp = g_{xx} \sim g_{yy} = 1.9924$). The difference in energy between the ${}^2A_1$ and ${}^2A_2$ states is small and the third term in the g_{xx} value is therefore negligible, in agreement with the scheme of Fig. 6b indicating a spin-pairing in the a_1' level.

Assuming a value of 170 cm^{-1} for λ, we calculate $E(^2B_1) - E(^2B_2) =$ 14000 cm^{-1} and $E(^2A_1) - E(^2B_2) \sim E(^2A_2) - E(^2B_2) = 34000$ cm^{-1}. These values correspond to electronic transitions but the optical spectrum of the $(C_8H_8)_2V$ complex does not show characteristic absorption bands in the visible region (Fig. 4). It is therefore not possible to ascertain, for such a ligand field, the spin—orbit coupling constant and therefore the importance of the electronic distribution in the molecular orbitals of the $(C_8H_8)_2V$ complex.

Moreover, the magnitude of the ^{51}V hyperfine coupling constants allows us to suggest that the unpaired electron is heavily localized on the metal. Our previous estimates of the *g*-factors calculated with assumption of such strong localization of the unpaired electron are consequently justified and the model of the crystal field is therefore satisfactory.

Experimental

The dicyclooctatetraenyl-titanium and -vanadium complexes have been prepared by the method of Goffart et al. [13]. Another sample of dicyclooctatetraenylvanadium was kindly supplied by Prof. Dr. G. Wilke who has synthesized the complex by a completely different method [14]. The two complexes show the same and typical infrared spectra in the 200-3500 cm^{-1} spectral range [7] and the elementary analyses correspond exactly to the molecular formula.

Magnetic susceptibility was measured from 4.2 to 300 K on a powder sample of $(C_8H_8)_2V$. The χ^{-1} versus temperature plot was linear within experimental error and extrapolated close to zero, indicating a normal Curie or Curie—Weiss temperature dependence.

Electron paramagnetic resonance spectra were recorded on a Varian E-12 spectrometer (X-band) in various conditions: from the solid itself, from a dilute solution in benzene at 300 K and from the same solution frozen at 77 K. The magnetic field is modulated at 100 kHz and the spectra were obtained as a first derivative of the signal. Spectra were calibrated using external DPPH ($g = 2.0037$) and the $g_\parallel$ and $g_\perp$-values were determined by the method of Lebedev [15].

The EPR parameters of the $(C_8H_8)_2V$ compound prepared in our laboratory by the method of Goffart or obtained from Wilke are exactly the same, but they are in contradiction with the previous results reported by Thomas and Hayes [9].

The spectra of the frozen solution sample show a main centre line and eight weak satellite lines (Fig. 3); these satellites correspond to the same species as the main line and not to another complex (resulting, for instance, from air oxidation of the former). This conclusion is supported by the following experiment: the paramagnetic resonance spectrum of a partially-oxidized sample of $(C_8H_8)_2V$ is a superposition of two spectra; one is the typical $(C_8H_8)_2V$ EPR spectrum and the other shows eight lines centred on a completely different $g_\parallel$-value from the first, thus indicating a different paramagnetic species.

Electronic spectra of the compounds in benzene solution were recorded with a Cary model 17 spectrometer.

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