

## ON THE CHEMISTRY OF "SANDWICH" COMPLEXES. XVI.\*

THE LIGAND FIELD THEORY FOR DICYCLOPENTADIENYL  $d^3$  AND  $d^7$  COMPLEXES. THE  $d-d$  TRANSITIONS AND LIGAND FIELD PARAMETERS OF VANADOCENE AND SOME COMPLEXES OF Cr(III)

I. PAVLÍK, V. ČERNÝ and E. MAXOVÁ

*Department of General and Inorganic Chemistry,  
Institute of Chemical Technology, Pardubice**Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.*

Received November 28th, 1969

Employing the approximation of the strong and the weak fields (Racah's method of irreducible tensors) and neglecting the spin-orbital coupling, the energies of the electron levels have been calculated with the aid of an axial ligand field of the  $D_{\infty h}$  symmetry for metallocenes with central  $d^3$  and  $d^7$  ions. The energy matrices are given for all the quartet and the doublet terms; the courses of the terms for different values of the splitting parameters  $D_s$ ,  $D_t$  are illustrated graphically. The paper also presents Tables of the Clebsch-Gordan coefficients for the group  $D_{\infty h}$  and the  $g^n$ -coefficients (for  $l = 2$ ,  $k = 4$ ,  $n = 3, 4, 5$ ). According to the ligand field theory the ground state of  $d^3$ -metallocenes is  ${}^4A_{2g}(e_{2g}^2 a_{1g}^1)$  and the ground state of  $d^7$ -metallocenes is  ${}^2E_{1g}(e_{2g}^4 a_{1g}^2 e_{1g}^1)$ . The theoretical results have been employed to interpret the  $d-d$  transitions in the electronic spectra of vanadocene  $V(C_5H_5)_2$ , the chromicinium cation  $Cr(C_5H_5)_2^+$  and carborane sandwich complexes of Cr(III). From the spectral data of these compounds the ligand field parameters have been calculated. On the basis of these parameters the bonding in these complexes is discussed and compared with that in ferrocene and nickelocene. The central atoms of the compared sandwich complexes in an axial ligand field can be ordered into a spectrochemical series,  $Fe(II) > Cr(III) > V(II) > Ni(II)$ , and into a nephelauxetic one:  $Ni(II) \approx Cr(III) \cong V(II) > Fe(II)$ . The spectral data also give information on the dicarbollide ligand and make possible its comparison with cyclopentadienyl.

In theoretical research into the nature of the covalent bonding in metallocenes, *i.e.* dicyclopentadienyl complexes of transition metals, little attention has been paid to the  $d^3$ -systems, such as vanadocene  $V(C_5H_5)_2$  or the chromicinium cation  $Cr(C_5H_5)_2^+$ , and  $d^7$ -systems, *e.g.* cobaltocene  $Co(C_5H_5)_2$ , the nickelocinium cation  $Ni(C_5H_5)_2^+$ . Šustorovič and Djatkina<sup>1,2</sup> attempted to elucidate the electronic structure of  $V(C_5H_5)_2$ ,  $Co(C_5H_5)_2$  and  $Ni(C_5H_5)_2^+$  by the semiquantitative MO-LCAO-SCF method. Since the presence of unpaired electrons in the studied particles made the calculations very difficult the authors had to put up with the determination of the ground state orbital configuration and with an estimate of electron density distribution in the metallocene complex. Recent semiempirical MO calculations (the extended Hückel method in the Wolfsberg-

\* Part XV: This Journal 35, 3045 (1970).

Helmholtz approximation) for vanadocene<sup>3-5</sup> and cobaltocene<sup>5</sup> have yielded information on the relative order, shape and localization of the oneelectron MO-shells.

To attack some problems of the electronic structure of metallocenes and account for their optical and magnetic properties it is possible to use the ligand field theory, which has recently been successfully applied to ferrocene  $\text{Fe}(\text{C}_5\text{H}_5)_2$  and nickelocene  $\text{Ni}(\text{C}_5\text{H}_5)_2$ , *i.e.* to the  $d^6$ - and  $d^8$ -systems<sup>6-8</sup>. With the dicyclopentadienyl  $d^3$ - and  $d^7$ -complexes this theory has not yet been employed and the present paper is an attempt at its application to them. An incomplete calculation for the  $d^3$ -system has been reported by Prins and van Voorst<sup>4,6</sup>. On the basis of their knowledge of the order of the  $d$ -shells, determined by MO-calculations, these authors have employed the method of a strong field with restricted configurational interaction and calculated the energies of several low-lying quartet and doublet terms. The obtained theoretical results will be employed to interpret the  $d-d$  spectra of some  $d^3$ -complexes, *viz.* vanadocene  $\text{V}(\text{C}_5\text{H}_5)_2$ , the chromicinium cation  $\text{Cr}(\text{C}_5\text{H}_5)_2^+$  and two carborane complexes of Cr(III):  $[\text{Cr}(\pi\text{-}(3)\text{-}1,7\text{-B}_9\text{C}_2\text{H}_{11})_2]^-$  and  $\text{C}_5\text{H}_5\text{Cr}(\pi\text{-}(3)\text{-}1,7\text{-B}_9\text{C}_2\text{H}_{11})$ .

Vanadocene, forming dark-violet monoclinic crystals, is very sensitive to oxygen. Its molecule, like those of the other metallocenes of the first transition series, has a pentagonal antiprismatic structure (symmetry point group  $D_{5d}$ )<sup>10</sup>. The magnetic moment  $\mu_{\text{eff}} = 3.84 \pm 0.04\mu_{\text{B}}$  (ref.<sup>9</sup>) suggests the presence of three unpaired electrons. Recent studies on the EPR spectra of vanadocene<sup>4,6,11</sup> have yielded a number of important findings on the nature of a covalent bond. An essential finding is that the order of the lowest antibonding and the highest bonding molecular orbitals of vanadocene is  $e_{1g} > a_{1g} > e_{2g}$ , and that the character of these orbitals is similar to that of the  $d$ -orbital of a metal. The existing experimental data on the electronic absorption spectrum of vanadocene<sup>4,6,12</sup> are incomplete (the part of the near infrared region is lacking) and not quite accurate (analysis of the absorption curve was omitted). The three normal  $d-d$  bands between 15000 and 25000  $\text{cm}^{-1}$  have recently been assigned and analysed by a procedure formally analogous to the strong field method with restricted configurational interaction<sup>4,6</sup>.

The chromicinium cation,  $[\text{Cr}(\text{C}_5\text{H}_5)_2]^+$  is paramagnetic. Its magnetic moment  $\mu_{\text{eff}} = 3.87\mu_{\text{B}}$  (ref.<sup>13</sup>) is practically the spin-only value for three unpaired electrons. The infrared spectrum of the complex corroborates its sandwich structure<sup>13</sup>.

Recent publications<sup>14</sup> describe sandwich complexes of the general formulae  $[\text{M}^{n+}(\text{Cb})_2]^{n-4}$  and  $[(\text{C}_5\text{H}_5)\text{M}^{n+}(\text{Cb})]^{n-3}$ , where  $\text{Cb}^{2-}$  designates the carborane ligand  $[(3)\text{-}1,2\text{-B}_9\text{C}_2\text{H}_{11}]^{2-}$  or its isomer  $[(3)\text{-}1,7\text{-B}_9\text{C}_2\text{H}_{11}]^{2-}$  and  $\text{M}^{n+}$  the transition metal ion. The anion  $\text{Cb}^{2-}$ , which has been given the name dicarbollide anion<sup>14</sup>, has the shape of an incomplete icosahedron (eleven points of this icosahedron are occupied by BH and CH groups, the remaining, twelfth point at position 3 is vacant). The "sandwich" part of the anion, represented by a quasipentagonal face  $\text{B}_3\text{C}_2\text{H}_5$  lying under the vacant position, can be regarded as an analogue of cyclopentadienyl,  $\text{C}_5\text{H}_5$ —. In 1968 a number of carborane complexes of Cr(III) were prepared (the

carborane analogues of chromicinium<sup>15</sup>). For the purpose of our study we have chosen complexes containing the ligand  $[(3)-1,7-B_9C_2H_{11}]^{2-}$ , because their electronic spectra, especially in the long-wave region, are well known<sup>15</sup>; complexes with the isomeric ligand are not suitable because the  $d-d$  bands of their spectra are not sufficiently resolved).

## THEORETICAL

The problem to be solved is the effect of the ligand field of two cyclopentadienyl ( $C_5H_5^-$ ) ligands on the central  $d^3$ - or  $d^7$ -ion. On disregarding the spin-orbit coupling the effect of such a field is described by the Hamiltonian

$$H = \sum_{i=1}^n \left\{ -\frac{\hbar^2}{2m} \Delta_i^2 - \frac{Ze^2}{r_i} \right\} + \sum_{i < j} \frac{e^2}{r_{ij}} + V_{LF},$$

where  $i$  designates the  $i$ -th  $d$ -electron of the central ion and  $V_{LF}$  the potential energy of  $d$ -electrons of the central ion in the ligand field. It has been proved<sup>7-9</sup> that dicyclopentadienyl sandwich complexes of transition metals whose isolated molecules have an effective  $D_{5d}$  or  $D_{5h}$  symmetry can be described by a ligand field of the axial symmetry  $D_{\infty h}$ . For a field of this symmetry the potential term  $V_{LF}$  can be expanded into a series of spherical harmonics  $Y_l^m$  as follows (the series includes only the terms contributing to the matrix elements);

$$V_{LF} = \sum_{i=i}^n \left\{ 4\sqrt{\pi} \frac{1}{r_{>}} Y_0^0(i) + 2 \left( \sqrt{\frac{\pi}{5}} \right) \frac{r_{<}^2}{r_{>}^3} (3 \cos^2 \alpha - 1) Y_2^0(i) + \right. \\ \left. + \frac{\sqrt{\pi}}{2} \frac{r_{<}^4}{r_{>}^5} \left( \frac{35}{3} \cos^4 \alpha - 10 \cos^2 \alpha + 1 \right) Y_4^0(i) \right\}; \quad (1)$$

here  $\alpha$  designates the azimuthal angle between the circularly spread ligand charge and the quantitation axis (the product of the ligand and the electron charges equals unity). The first term on the right-hand side of equation (1) has a spherical symmetry, so that it does not contribute to the splitting in the ligand field. The existence of the next two terms shows that an axial ligand field is described by two parameters,  $D_s$  and  $D_t$  (cf.<sup>17</sup>) defined as follows

$$D_s = \frac{1}{7} (3 \cos^2 \alpha - 1) \left\langle \frac{r_{<}^2}{r_{>}^3} \right\rangle; \\ D_t = -\frac{1}{28} \left( \frac{35}{3} \cos^4 \alpha - 10 \cos^2 \alpha + 1 \right) \left\langle \frac{r_{<}^4}{r_{>}^5} \right\rangle;$$

where  $\langle r^1/r^{1+1} \rangle$  denotes the mean value.

Since the field is axially symmetrical, the quantity  $\pm m_l$  remains to be a good quantum number; hence it follows that  $l$ .  $d$ -orbital functions differing in  $\pm m_l$  are not mixed, 2. bases of the five  $d$ -orbitals split into three series (with respect to  $m_l$ ), characterised by irreducible representations of the point group  $D_{\infty h}$ :

$$\begin{aligned} a_{1g} \quad m_l &= 0 & d_0(d_z^2), \\ e_{1g} \quad m_l &= \pm 1 & d_{\pm 1}(d_{xz}; d_{yz}), \\ e_{2g} \quad m_l &= \pm 2 & d_{\pm 2}(d_{x^2-y^2}; d_{xy}). \end{aligned}$$

Their one-electronic energies  $\langle m_l | \mathbf{V}_{LF} / m_l \rangle$ , which can be calculated from equation (1) by the standard procedure<sup>18</sup>, are<sup>17</sup> (the constant term is omitted):

$$\begin{aligned} E(a_{1g}) &= \langle 0 | \mathbf{V}_{LF} | 0 \rangle \approx 2Ds - 6Dt, \\ E(e_{1g}) &= \langle 1 | \mathbf{V}_{LF} | 1 \rangle \approx Ds + 4Dt, \\ E(e_{2g}) &= \langle 2 | \mathbf{V}_{LF} | 2 \rangle \approx -2Ds - Dt. \end{aligned} \quad (2)$$

Consequently, the three series of  $d$ -orbitals in an axial field have three different energies. Since with the dicyclopentadienyl complexes the actual value of the angle  $\alpha$  makes the parameters  $Ds$  and  $Dt$  always positive, the  $d$ -orbital  $e_{1g}$  is the energetically highest one; the relative order of the lower orbitals  $a_{1g}$  and  $e_{2g}$  depends in a given case on the actual values of the parameters  $Ds$  and  $Dt$  (on their ratio  $Ds/Dt$ ). For  $E(e_{2g}) = E(a_{1g})$  this ratio equals 1.25; for  $Ds/Dt > 1.25$  it holds that  $E(a_{1g}) > E(e_{2g})$  and *vice versa*. A polyelectronic problem (the  $d^3$ - or  $d^7$ -problem) can be solved by the strong field or the weak field method.

*A strong ligand field.* In the case of a strong ligand field the effect of the operator  $\mathbf{V}_{LF}$  outweighs the interelectron repulsion, i.e.  $\mathbf{V}_{LF} > \sum_{i < j} (e^2/r_{ij})$ . The one-electronic wave functions ( $\gamma\lambda$ ) pertaining to the irreducible representations  $\Gamma$  of the point group  $D_{\infty h}$  and derived from the functions  $|l m_l\rangle$  are:

$$\begin{aligned} |a_{1g}^t\rangle &\equiv |z^2\rangle &= |2 0\rangle \equiv a, \\ |e_{1g}^c\rangle &\equiv |xz\rangle &= -2^{-1/2}\{|2 1\rangle - |2 -1\rangle\} \equiv \beta, \\ |e_{1g}^s\rangle &\equiv |yz\rangle &= i \cdot 2^{-1/2}\{|2 1\rangle + |2 -1\rangle\} \equiv \epsilon, \\ |e_{2g}^c\rangle &\equiv |x^2 - y^2\rangle &= 2^{-1/2}\{|2 2\rangle + |2 -2\rangle\} \equiv \zeta, \\ |e_{2g}^s\rangle &\equiv |xy\rangle &= -i \cdot 2^{-1/2}\{|2 2\rangle - |2 -2\rangle\} \equiv \eta \end{aligned}$$

$\lambda$  is a quantum number, specifying which component in the basis of the  $\Gamma$  representation the given function is;  $c$  denotes that the function is transformed by rotation  $\mathbf{C}_\alpha(z)$  as  $\cos m\psi$ ;  $s$  analogously denotes transformation as  $\sin m\psi$ ;  $t$  designates a one-dimensional representation.

The polyelectronic wave functions  $|(\gamma_1^{n_1} \gamma_2^{n_2} \gamma_3^{n_3})^{2S+1} \Gamma, M_S \lambda\rangle$  can be written according to Griffith<sup>18</sup> with the aid of the wave functions  $|(\gamma_1^{n_1})^{2S+1} \Gamma, M_S \lambda\rangle$  (Table I) and the Clebsch-Gordan coefficients  $\langle \Gamma_1 \Gamma_2 \lambda_1 \lambda_2 | \Gamma \lambda \rangle$  for the point group  $D_{\infty h}$ <sup>18,19</sup> (Table II); the nonzero values which are not included can be obtained from the symmetry properties, defined<sup>19</sup> as:

$$\begin{aligned} \langle \Gamma_1 \Gamma_2 \gamma_1 \gamma_2 | \Gamma \gamma \rangle &= (-1)^{\Gamma_1 + \Gamma_2 + \Gamma} \langle \Gamma_2 \Gamma_1 \gamma_2 \gamma_1 | \Gamma \gamma \rangle = \\ &= (-1)^{\Gamma_1 + \Gamma_2 + \Gamma} \left[ \frac{\lambda(\Gamma)}{\lambda(\Gamma_2)} \right]^{1/2} \langle \Gamma_1 \Gamma_1 \gamma_1 \gamma | \Gamma_2 \gamma_2 \rangle, \end{aligned}$$

here  $(-1)^{\Gamma} = -1$  for  $\Gamma = A_2$  and  $(-1)^{\Gamma} = 1$  for the other  $\Gamma$  values;  $\lambda(\Gamma)$  equals the dimension of the representation. To the symbols of the representations in Table II can be attached the indices  $g$  and  $u$ , according to the rules  $g \cdot g = u$ ,  $u \cdot u = g$ ,  $g \cdot u = u$ ,  $u \cdot g = g$ , and the coefficients

$\langle S_1 S_2 M_{S_1} M_{S_2} | S M_S \rangle$  are given in<sup>20,21</sup>. In this way we obtained the wave functions of a  $d^3$  system in an axial field  $D_{\infty h}$  (Table III). From these we calculated the matrix elements of the operator  $\mathbf{H}$ , given in Table IV (the matrix elements are diagonal in respect to  $\mathbf{V}_{LF}$ ; the elements for the interelectron repulsion operator were calculated<sup>18,20</sup> from tabulated integrals  $\langle ab || r_{12} || cd \rangle$ , where  $a, b, c, d$  are some of the wave functions  $a, \vartheta, \varepsilon, \xi, \eta$ ).

*A weak ligand field.* In this case the interelectron repulsion dominates over the effect of the ligand field, i.e.  $\sum_{i < j} (e^2 / r_{ij}) > \mathbf{V}_{LF}$ . The free  $d^3$ - and  $d^7$ -ions have two quartet terms,  ${}^4F$  and  ${}^4P$ , and six doublet terms,  ${}^2H, {}^2G, {}^2F, {}^2D, {}^2D, {}^2P$ , associated with the wave functions  $|(d^3) v S L M_S M_L \rangle$

TABLE I

Wave Functions  $|(y^n)^{2S+1} \Gamma, M_S \lambda \rangle$  for the Point Group  $D_{\infty h}$

The wave functions are arranged according to the conventions published<sup>19</sup> for the Clebsch-Gordan coefficients  $\langle \Gamma_1 \Gamma_2 \lambda_1 \lambda_2 | \Gamma \lambda \rangle$  and genealogical coefficients  $\langle \gamma^m(S_1 \Gamma_1), \gamma^n(S_2 \Gamma_2) | \gamma^m + n S \Gamma \rangle$ .

Wave function	Wave function
$ (a^1_g)^2 A_{1g}, \frac{1}{2} \iota \rangle = a^+$	$ (e^4_g)^1 A_{1g}, 0 \iota \rangle =  \vartheta^+ \vartheta^- \varepsilon^+ \varepsilon^- $
$ (a^2_g)^1 A_{1g}, 0 \iota \rangle =  a^+ a^- $	$ (e^2_g)^2 E_{2g}, \frac{1}{2} c \rangle = \xi^+$
$ (e^1_g)^2 E_{1g}, \frac{1}{2} c \rangle = \vartheta^+$	$ (e^1_g)^2 E_{2g}, \frac{1}{2} s \rangle = \eta^+$
$ (e^1_g)^2 E_{1g}, \frac{1}{2} s \rangle = \varepsilon^+$	$ (e^2_g)^3 A_{2g}, 1 \iota \rangle =  \xi^+ \eta^+ $
$ (e^2_g)^3 A_{2g}, 1 \iota \rangle =  \vartheta^+ \varepsilon^+ $	$ (e^2_g)^1 A_{1g}, 0 \iota \rangle = 2^{-1/2} \{  \xi^+ \xi^-  +  \eta^+ \eta^-  \}$
$ (e^2_g)^1 A_{1g}, 0 \iota \rangle = 2^{-1/2} \{  \vartheta^+ \vartheta^-  +  \varepsilon^+ \varepsilon^-  \}$	$ (e^2_g)^1 E_{4g}, 0 c \rangle = 2^{-1/2} \{  \xi^+ \xi^-  -  \eta^+ \eta^-  \}$
$ (e^2_g)^1 E_{2g}, 0 c \rangle = 2^{-1/2} \{  \vartheta^+ \vartheta^-  -  \varepsilon^+ \varepsilon^-  \}$	$ (e^2_g)^1 E_{4g}, 0 s \rangle = 2^{-1/2} \{  \xi^+ \eta^-  +  \eta^+ \xi^-  \}$
$ (e^2_g)^1 E_{2g}, 0 s \rangle = 2^{-1/2} \{  \vartheta^+ \varepsilon^-  +  \varepsilon^+ \vartheta^-  \}$	$ (e^2_g)^2 E_{2g}, \frac{1}{2} c \rangle =  \xi^+ \eta^+ \eta^- $
$ (e^2_g)^1 E_{2g}, \frac{1}{2} c \rangle =  \vartheta^+ \varepsilon^+ \varepsilon^- $	$ (e^2_g)^2 E_{2g}, \frac{1}{2} s \rangle =  \xi^+ \xi^- \eta^+ $
$ (e^2_g)^1 E_{1g}, \frac{1}{2} c \rangle =  \vartheta^+ \vartheta^- \varepsilon^+ $	$ (e^4_g)^1 A_{1g}, 0 \iota \rangle =  \xi^+ \xi^- \eta^+ \eta^- $
$ (e^2_g)^1 E_{1g}, \frac{1}{2} s \rangle =  \vartheta^+ \vartheta^- \varepsilon^- $	

TABLE II

Nonzero Clebsch-Gordan Coefficients for the Point Group  $D_{\infty h}$

$\Gamma_1$	$\Gamma_2$	$\Gamma$	$\gamma_1$	$\gamma_2$	$\gamma$	$\langle \Gamma_1 \Gamma_2 \gamma_1 \gamma_2   \Gamma \gamma \rangle$
$A_1$	$\Gamma$	$\Gamma$	$\iota$	$\gamma$	$\gamma$	1
$A_2$	$E_m$	$E_m$	$\iota$	$c$	$s$	1
			$\iota$	$s$	$c$	-1
			$c$	$c$	$c$	} $2^{-1/2}$
			$c$	$s$	$s$	
$E_m$	$E_{m'}$	$E_{(m+m')}$	$s$	$c$	$s$	
			$s$	$s$	$c$	

or  $(d^7) vSLM_S M_L$ ;  $v$  is the so-called seniority number. The energies of the terms expressed by Racah parameters  $B$  and  $C$  have been published<sup>18,22</sup>.

In an axial ligand field  $D_{\infty h}$  the terms of a free ion  $d^3$  ( $d^7$ ) split as follows:

$$2S+1L \rightarrow 2S+1A_{k_g} + \sum_{M=1}^L 2S+1E_{M_g}; \quad \begin{array}{l} k=1 \text{ for } L=2p, \\ k=2 \text{ for } L=2p+1, \\ p=0, 1, 2. \end{array}$$

TABLE III

Wave Functions  $|\gamma_1^{n_1} \gamma_2^{n_2} \gamma_3^{n_3}\rangle^{2S+1} \Gamma, M_S \lambda\rangle$  of a  $d^3$ -System for the Point Groups  $D_{\infty h}$

## Wave function

- $$\begin{aligned} |1\rangle &\equiv |(e_{2g}^2 \sigma_{1g}^1)^2 A_{1g}, \frac{1}{2}\rangle = 2^{-1/2} \{ |a^+ \xi^+ \xi^-| + |a^+ \eta^+ \eta^-| \} \\ |2\rangle &\equiv |(e_{2g}^2 \sigma_{1g}^1)^4 A_{2g}, \frac{3}{2}\rangle = |a^+ \xi^+ \eta^+| \\ |3\rangle &\equiv |(e_{2g}^2 \sigma_{1g}^1)^2 A_{2g}, \frac{1}{2}\rangle = 6^{-1/2} \{ 2|\xi^+ \eta^+ a^-| + |\xi^+ a^+ \eta^-| + |a^+ \eta^+ \xi^-| \} \\ |4\rangle &\equiv |(e_{2g}^2 \sigma_{1g}^1)^2 E_{4g}, \frac{1}{2}c\rangle = 2^{-1/2} \{ |a^+ \xi^+ \xi^-| - |a^+ \eta^+ \eta^-| \} \\ |5\rangle &\equiv |(e_{2g}^2)^2 E_{2g}, \frac{1}{2}c\rangle = |\xi^+ \eta^+ \eta^-| \\ |6\rangle &\equiv |(e_{2g}^2 \sigma_{1g}^1)^2 E_{2g}, \frac{1}{2}c\rangle = |\xi^+ a^+ a^-| \\ |7\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1 e_{1g}^1)^4 E_{1g}, \frac{3}{2}c\rangle = 2^{-1/2} \{ |a^+ \xi^+ \vartheta^+| + |a^+ \eta^+ \varepsilon^+| \} \\ |8\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1 e_{1g}^1)^4 E_{3g}, \frac{3}{2}c\rangle = 2^{-1/2} \{ |a^+ \xi^+ \vartheta^+| - |a^+ \eta^+ \varepsilon^+| \} \\ |9\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1 [^3 E_{1g}], \sigma_{1g}^1)^2 E_{1g}, \frac{1}{2}c\rangle = 12^{-1/2} \{ 2|\xi^+ \vartheta^+ a^-| + 2|\eta^+ \varepsilon^+ a^-| + |\xi^+ a^+ \vartheta^-| + \\ &\quad + |a^+ \vartheta^+ \xi^-| + |\eta^+ \varepsilon^+ \eta^-| + |a^+ \varepsilon^+ \eta^-| \} \\ |10\rangle &\equiv |(e_{2g}^1 e_{1g}^1 [^1 E_{1g}], \sigma_{1g}^1)^2 E_{1g}, \frac{1}{2}c\rangle = 2^{-1} \{ |a^+ \xi^+ \vartheta^-| + |a^+ \vartheta^+ \xi^-| + |a^+ \eta^+ \varepsilon^-| + \\ &\quad + |a^+ \varepsilon^+ \eta^-| \} \\ |11\rangle &\equiv |(e_{2g}^1 e_{1g}^1 [^3 E_{3g}], \sigma_{1g}^1)^2 E_{3g}, \frac{1}{2}c\rangle = 12^{-1/2} \{ 2|\xi^+ \vartheta^+ a^-| + 2|\varepsilon^+ \eta^+ a^-| + |\xi^+ a^+ \vartheta^-| + \\ &\quad + |a^+ \vartheta^+ \xi^-| + |a^+ \eta^+ \varepsilon^-| + |\varepsilon^+ a^+ \eta^-| \} \\ |12\rangle &\equiv |(e_{2g}^1 e_{1g}^1 [^1 E_{3g}], \sigma_{1g}^1)^2 E_{3g}, \frac{1}{2}c\rangle = 2^{-1} \{ |a^+ \xi^+ \vartheta^-| + |a^+ \vartheta^+ \xi^-| + |\eta^+ a^+ \varepsilon^-| + \\ &\quad + |\varepsilon^+ a^+ \eta^-| \} \\ |13\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^4 E_{1g}, \frac{3}{2}c\rangle = |\eta^+ \xi^+ \varepsilon^+| \\ |14\rangle &\equiv |(e_{2g}^1 [^3 A_{2g}], e_{1g}^1)^2 E_{1g}, \frac{1}{2}c\rangle = 6^{-1/2} \{ 2|\eta^+ \xi^+ \varepsilon^-| + |\varepsilon^+ \xi^+ \eta^-| + |\eta^+ \varepsilon^+ \xi^-| \} \\ |15\rangle &\equiv |(e_{2g}^1 [^1 A_{1g}], e_{1g}^1)^2 E_{1g}, \frac{1}{2}c\rangle = 2^{-1/2} \{ |\vartheta^+ \xi^+ \xi^-| + |\vartheta^+ \eta^+ \eta^-| \} \\ |16\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^2 E_{3g}, \frac{1}{2}c\rangle = 2^{-1} \{ |\vartheta^+ \xi^+ \xi^-| - |\vartheta^+ \eta^+ \eta^-| + |\varepsilon^+ \xi^+ \eta^-| + |\varepsilon^+ \eta^+ \xi^-| \} \\ |17\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^2 E_{5g}, \frac{1}{2}c\rangle = 2^{-1} \{ |\vartheta^+ \xi^+ \xi^-| - |\vartheta^+ \eta^+ \eta^-| - |\varepsilon^+ \xi^+ \eta^-| - |\varepsilon^+ \eta^+ \xi^-| \} \\ |18\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^2 E_{1g}, \frac{1}{2}c\rangle = |\vartheta^+ a^+ a^-| \\ |19\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^4 E_{2g}, \frac{3}{2}c\rangle = |\vartheta^+ \eta^+ \varepsilon^+| \\ |20\rangle &\equiv |(e_{2g}^1 [^3 A_{2g}], e_{1g}^1)^2 E_{2g}, \frac{1}{2}c\rangle = 6^{-1/2} \{ 2|\varepsilon^+ \vartheta^+ \eta^-| - |\vartheta^+ \eta^+ \varepsilon^-| + |\varepsilon^+ \eta^+ \vartheta^-| \} \\ |21\rangle &\equiv |(e_{2g}^1 [^1 A_{1g}], e_{1g}^1)^2 E_{2g}, \frac{1}{2}c\rangle = 2^{-1/2} \{ |\xi^+ \vartheta^+ \vartheta^-| + |\xi^+ \varepsilon^+ \varepsilon^-| \} \\ |22\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^2 E_{4g}, \frac{1}{2}c\rangle = 2^{-1} \{ |\xi^+ \vartheta^+ \vartheta^-| - |\xi^+ \varepsilon^+ \varepsilon^-| + |\vartheta^+ \eta^+ \varepsilon^-| - |\eta^+ \varepsilon^+ \vartheta^-| \} \\ |23\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^2 A_{1g}, \frac{1}{2}c\rangle = 2^{-1} \{ |\xi^+ \vartheta^+ \vartheta^-| - |\xi^+ \varepsilon^+ \varepsilon^-| - |\vartheta^+ \eta^+ \varepsilon^-| + |\eta^+ \varepsilon^+ \vartheta^-| \} \\ |24\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^2 A_{2g}, \frac{1}{2}c\rangle = 2^{-1} \{ |\xi^+ \vartheta^+ \varepsilon^-| + |\xi^+ \varepsilon^+ \vartheta^-| - |\eta^+ \vartheta^+ \vartheta^-| + |\eta^+ \varepsilon^+ \varepsilon^-| \} \\ |25\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^4 A_{2g}, \frac{3}{2}c\rangle = |a^+ \vartheta^+ \varepsilon^+| \\ |26\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^2 A_{2g}, \frac{1}{2}c\rangle = 6^{-1/2} \{ 2|\vartheta^+ \varepsilon^+ a^-| - |a^+ \vartheta^+ \varepsilon^-| - |\varepsilon^+ a^+ \vartheta^-| \} \\ |27\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^2 A_{1g}, \frac{1}{2}c\rangle = 2^{-1/2} \{ |a^+ \vartheta^+ \vartheta^-| + |a^+ \varepsilon^+ \varepsilon^-| \} \\ |28\rangle &\equiv |(e_{2g}^1 \sigma_{1g}^1)^2 E_{2g}, \frac{1}{2}c\rangle = 2^{-1/2} \{ |a^+ \vartheta^+ \vartheta^-| - |a^+ \varepsilon^+ \varepsilon^-| \} \\ |29\rangle &\equiv |(e_{2g}^1)^2 E_{1g}, \frac{1}{2}c\rangle = |\vartheta^+ \varepsilon^+ \varepsilon^-| \end{aligned}$$

The wave functions  $|(d^3) vSLM_S \pm M\rangle$  are the bases of the irreducible representations  $E_{Mg}$ ; the function  $|(d^3) vSLM_S 0\rangle$  is the basis of the representation  $A_{kg}$ . The weak-field matrix elements  $\langle (d^3) vSLM_S M_L | \mathbf{V}_{LF} | (d^3) v'S'L'M_S' M_L' \rangle$  can in principle be calculated with the aid of the one-electronic energies (2) and of the functions  $|(d^3) vSLM_S M_L\rangle$ , given in Condon and Shortley's monograph<sup>23</sup> for  $L = 2$  and, for other  $L$  values, in ref.<sup>24</sup>.

Since this procedure is tedious and difficult to survey in the given case we calculated the weak field matrix elements by Racah's method of irreducible tensors, extended to apply to molecular systems<sup>19,25</sup>, which we supplemented with necessary data for the symmetry  $D_{\infty h}$ . Employing this method the matrix elements of the individual terms of a one-electron operator ( $I$ ) can be calculated from a simple formula (analogous to formulae 7 and 8 in ref.<sup>19</sup>):

$$\begin{aligned} & \langle (l^n) vSLM_S M_L | \sum_{i=1}^n a_{km} f_k(r_i) Y_k^m(\vartheta_i, \varphi_i) | (l^n) v'S'L'M_S' M_L' \rangle = \\ & = (-1)^{L-M_L} \delta_{SS'} \delta_{M_S M_S'} \begin{pmatrix} L & k & L' \\ -M_L & m & M_L' \end{pmatrix} g_{v'S'L', v'S'L'}^n(l, k) a_{km} \langle f_k(r) \rangle \langle l \| Y_k \| l \rangle; \quad (3) \end{aligned}$$

$a_{km}$  is a number,  $f_k(r)$  is a function of  $r$  (the product  $a_{km} \langle f_k(r) \rangle$  for operator ( $I$ ) equals  $14 \sqrt{[(\pi/5)Ds]}$  for  $k = 2$ ,  $m = 0$ , and  $-14 \sqrt{(\pi)Dt}$  for  $k = 4$ ,  $m = 0$ );  $\langle l \| Y_k \| l \rangle$  is a reduced matrix element<sup>24,25</sup>, which in the d-functions assumes the values

$$\langle 2 \| Y_2 \| 2 \rangle = -5/(14\pi)^{1/2}; \quad \langle 2 \| Y_4 \| 2 \rangle = 3 \cdot 35^{1/2}/7(2\pi)^{1/2}.$$

The  $3j$ -coefficients  $\begin{pmatrix} L & k & L' \\ -M_L & m & M_L' \end{pmatrix}$  are tabulated<sup>26</sup> and can also be calculated from the Clebsch-Gordan coefficients<sup>20,21</sup> with the aid of the relation

$$\begin{pmatrix} a & b & c \\ \alpha & \beta & -\gamma \end{pmatrix} = (-1)^{a-b+\gamma} \frac{\langle a\alpha b\beta | c\gamma \rangle}{(2c+1)^{1/2}};$$

$g_{v'S'L', v'S'L'}^n(l, k)$  are coefficients which can be calculated from genealogical coefficients<sup>25,21</sup>  $\langle \} \rangle$  and  $6j$ -coefficients<sup>25,26</sup>  $\{ \}$  according to the equation

$$\begin{aligned} & g_{v'S'L', v'S'L'}^n = \\ & n[(2L+1)(2L'+1)]^{1/2} \sum_{v_1, S_1, L_1} \langle l^n vSL \{ | l^{n-1}(v_1 S_1 L_1), l \} \rangle \langle l^{n-1}(v_1 S_1 L_1), l \rangle \cdot \\ & \cdot I^n v'S'L' \rangle \left\{ \begin{matrix} LL'k \\ llL_1 \end{matrix} \right\} (-1)^{L_1+L+1+k}. \end{aligned}$$

For these  $g^n$ -coefficients it applies that  $g_{v'S'L', v'S'L'}^n = (-1)^{L-L'} g_{v'S'L', v'S'L'}^n$ . Since in the available literature the  $g^n$  coefficients are tabulated<sup>27</sup> only for  $l = 2$ ,  $k = 2$  and  $n = 2, 3, 4, 5$  (under the heading  $(\alpha LS \| U^{(2)} \| \alpha' L'S')$ , we have calculated their values for  $l = 2$ ,  $k = 4$ ,  $n = 3, 4, 5$  (Table V).

This procedure transforms the calculation of weak field matrix elements into a summation of products of tabulated values. The matrix elements of the operator  $\mathbf{H}$  calculated by the weak field method for the  $d^3$ -system are listed in Table VI.

As matrices of the terms  $2S+1F$  for a weak and a strong field are connected by a unitary transformation their eigenvalues are identical. The strong field matrices for the terms of the  $d^7$ -system

TABLE IV  
 A  $d^3$ -System in a Axial Ligand Field  $D_{\infty h}$ : the Strong Field Matrices

${}^4A_{2g}$ :	$\begin{array}{c}  2\rangle \\ -2Ds - 8Dt - 12B \\ \hline 6B \\ 4Ds + 2Dt - 3B \end{array}$	$\begin{array}{c}  25\rangle \\ 6B \\ \hline 4Ds + 2Dt - 3B \end{array}$
${}^4E_{1g}$ :	$\begin{array}{c}  7\rangle \\ Ds - 3Dt - 9B \\ \hline -3\sqrt{(6)B} \\ -3Ds + 2Dt - 6B \end{array}$	$\begin{array}{c}  13\rangle \\ -3\sqrt{(6)B} \\ \hline -3Ds + 2Dt - 6B \end{array}$
${}^4E_{2g}$ :	$\begin{array}{c}  19\rangle \\ 7Dt - 15B \end{array}$	
${}^4E_{3g}$ :	$\begin{array}{c}  8\rangle \\ Ds - 3Dt - 15B \end{array}$	
${}^2E_{5g}$ :	$\begin{array}{c}  17\rangle \\ -3Ds + 2Dt - 6B + 3C \end{array}$	
${}^2E_{4g}$ :	$\begin{array}{c}  4\rangle \\ -2Ds - 8Dt - 8B + 3C \\ \hline -\sqrt{(6)B} \\ 7Dt - 9B + 3C \end{array}$	$\begin{array}{c}  22\rangle \\ -\sqrt{(6)B} \\ \hline 7Dt - 9B + 3C \end{array}$
${}^2E_{3g}$ :	$\begin{array}{c}  11\rangle \\ Ds - 3Dt - \frac{15}{2}B + 3C \\ \hline \frac{3}{2}\sqrt{(3)B} \\ Ds - 3Dt - \frac{1}{2}B + 3C \end{array}$	$\begin{array}{c}  12\rangle \\ \frac{3}{2}\sqrt{(3)B} \\ \hline Ds - 3Dt - \frac{1}{2}B + 3C \end{array}$
${}^2A_{2g}$ :	$\begin{array}{c}  3\rangle \\ -2Ds - 8Dt + 3C \\ \hline 3\sqrt{(2)B} \\ 7Dt - 3B + 3C \end{array}$	$\begin{array}{c}  24\rangle \\ 3\sqrt{(2)B} \\ \hline 7Dt - 3B + 3C \end{array}$
		$\begin{array}{c}  16\rangle \\ 6B \\ \hline 4\sqrt{(3)B} \\ -3Ds + 2Dt + 3C \end{array}$
		$\begin{array}{c}  26\rangle \\ 6B \\ \hline 3\sqrt{(2)B} \\ 4Ds + 2Dt + 3C \end{array}$



${}^2A_{1g}$	$\begin{array}{c}  1\rangle \\ -2Ds - 8Dt - 8B + 5C \\  23\rangle \\ -\sqrt{(6)B} \\ 7Dt - 3B + 3C \\  27\rangle \\ 6B + 2C \\ -5\sqrt{(6)B} \\ 4Ds + 2Dt + 10B + 5C \end{array}$
${}^2E_{2g}$	$\begin{array}{c}  5\rangle \\ -6Ds - 3Dt + 12B + 4C \\  6\rangle \\ 4B + C \\ 2Ds - 13Dt - 8B + 4C \\  20\rangle \\ -3\sqrt{(6)B} \\ 7Dt - 6B + 3C \\  21\rangle \\ \sqrt{(2)(3B+C)} \\ \sqrt{(2)(B+C)} \\ -3\sqrt{(3)B} \\ 7Dt + 5C \\  28\rangle \\ 0 \\ -\sqrt{(6)B} \\ 3B \\ -5\sqrt{(3)B} \\ 4Ds + 2Dt + 4B + 3C \end{array}$
${}^2E_{1g}$	$\begin{array}{c}  9\rangle \\ Ds - 3Dt - \frac{3}{2}B + 3C \\  10\rangle \\ \frac{3}{2}\sqrt{(3)B} \\ Ds - 3Dt - \frac{13}{2}B + 3C \\  14\rangle \\ 0 \\ -3\sqrt{(2)B} \\ -3Ds + 2Dt + 3B + 3C \\  15\rangle \\ 3\sqrt{(2)B} \\ 2\sqrt{(6)B} \\ -3\sqrt{(3)B} \\ -3Ds + 2Dt - 3B + 5C \\  18\rangle \\ 9B \\ \sqrt{(3)B} \\ 0 \\ \sqrt{(2)(4B+C)} \\ 5Ds - 8Dt + 7B + 4C \\  29\rangle \\ 3B \\ \sqrt{(3)B} \\ -3\sqrt{(6)B} \\ \sqrt{(2)(3B+C)} \\ B + C \\ 3Ds + 12Dt - 3B + 4C \end{array}$

TABLE V

Nonzero Values of the Coefficients  $g_{v'SL, v'S'L}^n(l, k)$  for  $l = 2, k = 4, n = 3, 4, 5$ 

$2S + \frac{1}{2}L \rightarrow$ $\rightarrow 2S' + \frac{1}{2}L'$	$g$	$2S + \frac{1}{2}L \rightarrow$ $\rightarrow 2S' + \frac{1}{2}L'$	$g$
$n = 3$			
${}^4_3P \rightarrow {}^4_3F$	$\sqrt{(2)}/\sqrt{5}$	${}^3_4F \rightarrow {}^3_4F$	$\sqrt{(11)}/2\sqrt{5}$
${}^4_3F \rightarrow {}^4_3F$	$\sqrt{(11)}/\sqrt{5}$	${}^3_4G \rightarrow {}^3_4G$	$-\sqrt{(33)}/6\sqrt{35}$
${}^2_3P \rightarrow {}^2_3F$	$11\sqrt{(35)}/70$	${}^3_4H \rightarrow {}^3_4H$	$-\sqrt{(11)}/\sqrt{(13)}/2\sqrt{35}$
${}^2_3G \rightarrow {}^2_3G$	$-3\sqrt{(15)}/10\sqrt{7}$	${}^1_4G \rightarrow {}^1_4G$	$-3\sqrt{(11)}/\sqrt{(13)}/14\sqrt{5}$
${}^2_3H \rightarrow {}^2_3H$	$\sqrt{(22)}/\sqrt{35}$	${}^1_4H \rightarrow {}^1_4H$	$\sqrt{(3)}/\sqrt{(11)}/\sqrt{(13)}/6\sqrt{35}$
${}^1_2D \rightarrow {}^1_2D$	$1/2$	${}^1_4S \rightarrow {}^1_4S$	$2\sqrt{(11)}/\sqrt{(13)}/3\sqrt{35}$
${}^2_3D \rightarrow {}^2_3D$	$-5\sqrt{(3)}/6\sqrt{7}$	${}^1_4G \rightarrow {}^1_4G$	$\sqrt{(6)}/\sqrt{5}$
${}^2_3F \rightarrow {}^2_3F$	$-\sqrt{(5)}/\sqrt{6}$	${}^1_4S \rightarrow {}^1_4S$	$-\sqrt{(10)}/3\sqrt{7}$
${}^2_3G \rightarrow {}^2_3G$	$\sqrt{(11)}/\sqrt{14}$	${}^1_4G \rightarrow {}^1_4G$	$2\sqrt{(22)}/3\sqrt{35}$
${}^2_3H \rightarrow {}^2_3H$	$\sqrt{(11)}/\sqrt{6}$	${}^1_2D \rightarrow {}^1_2D$	$4/21$
${}^2_3D \rightarrow {}^2_3D$	$-19/42$	${}^1_4D \rightarrow {}^1_4D$	$10\sqrt{(2)}/21$
${}^2_3F \rightarrow {}^2_3F$	$-\sqrt{(10)}/3\sqrt{7}$	${}^1_4F \rightarrow {}^1_4F$	$-\sqrt{(14)}/3$
${}^2_3G \rightarrow {}^2_3G$	$-\sqrt{(66)}/7$	${}^1_2G \rightarrow {}^1_2G$	$\sqrt{(110)}/21$
${}^2_3H \rightarrow {}^2_3H$	$-\sqrt{(11)}/3\sqrt{14}$	${}^1_4G \rightarrow {}^1_4G$	$\sqrt{(10)}/21$
${}^2_3F \rightarrow {}^2_3F$	$\sqrt{(11)}/6\sqrt{5}$	${}^1_4I \rightarrow {}^1_4I$	$-2\sqrt{(13)}/3\sqrt{7}$
${}^2_3G \rightarrow {}^2_3G$	$-\sqrt{(33)}/2\sqrt{35}$	${}^1_4D \rightarrow {}^1_4D$	$-16/21$
${}^2_3H \rightarrow {}^2_3H$	$\sqrt{(11)}/\sqrt{(13)}/6\sqrt{35}$	${}^1_4F \rightarrow {}^1_4F$	$-\sqrt{(7)}/42$
${}^2_3G \rightarrow {}^2_3G$	$-\sqrt{(11)}/\sqrt{(13)}/14\sqrt{5}$	${}^1_2G \rightarrow {}^1_2G$	$-2\sqrt{(55)}/21$
${}^2_3H \rightarrow {}^2_3H$	$-\sqrt{(3)}/\sqrt{(11)}/\sqrt{(13)}/2\sqrt{35}$	${}^1_4G \rightarrow {}^1_4G$	$-13\sqrt{(5)}/42$
${}^2_3H \rightarrow {}^2_3H$	$-\sqrt{(11)}/\sqrt{(13)}/3\sqrt{35}$	${}^1_4I \rightarrow {}^1_4I$	$\sqrt{(26)}/3\sqrt{7}$
$n = 4$			
${}^5_4D \rightarrow {}^5_4D$	$-1$	${}^1_4F \rightarrow {}^1_4F$	$-\sqrt{(11)}/6\sqrt{5}$
${}^3_2P \rightarrow {}^3_2F$	$-\sqrt{(10)}/15$	${}^1_4G \rightarrow {}^1_4G$	$3\sqrt{(5)}/2\sqrt{7}$
${}^3_2F \rightarrow {}^3_2F$	$\sqrt{(10)}/3$	${}^1_4I \rightarrow {}^1_4I$	$\sqrt{(7)}/\sqrt{(13)}/6\sqrt{5}$
${}^3_2G \rightarrow {}^3_2G$	$-\sqrt{(6)}/3\sqrt{5}$	${}^1_2G \rightarrow {}^1_2G$	$\sqrt{(11)}/\sqrt{(13)}/21\sqrt{5}$
${}^3_2H \rightarrow {}^3_2H$	$-2\sqrt{(11)}/3\sqrt{5}$	${}^1_4G \rightarrow {}^1_4G$	$-4\sqrt{(5)}/\sqrt{(13)}/21$
${}^3_2P \rightarrow {}^3_2P$	$2\sqrt{(5)}/3\sqrt{7}$	${}^1_4I \rightarrow {}^1_4I$	$2\sqrt{(5)}/\sqrt{(13)}/3\sqrt{7}$
${}^3_2F \rightarrow {}^3_2F$	$-\sqrt{(5)}/30\sqrt{7}$	${}^1_4G \rightarrow {}^1_4G$	$17\sqrt{(13)}/42\sqrt{55}$
${}^3_2G \rightarrow {}^3_2G$	$17\sqrt{(15)}/30\sqrt{7}$	${}^1_4I \rightarrow {}^1_4I$	$-5\sqrt{(5)}/\sqrt{(13)}/6\sqrt{(77)}$
${}^3_2H \rightarrow {}^3_2H$	$\sqrt{(22)}/3\sqrt{35}$	${}^1_4I \rightarrow {}^1_4I$	$-2\sqrt{(2)}/\sqrt{(13)}/\sqrt{(17)}/3\sqrt{55}$
${}^3_2D \rightarrow {}^3_2D$	$-11/21$	$n = 5$	
${}^3_2F \rightarrow {}^3_2F$	$-2\sqrt{(10)}/3\sqrt{7}$	${}^4_3P \rightarrow {}^4_3G$	$\sqrt{2}$
${}^3_2G \rightarrow {}^3_2G$	$-\sqrt{(10)}/2\sqrt{7}$	${}^5_4D \rightarrow {}^5_4F$	$-\sqrt{(10)}/\sqrt{7}$
${}^3_2H \rightarrow {}^3_2H$	$\sqrt{(66)}/14$	${}^4_3F \rightarrow {}^4_3G$	$\sqrt{(11)}/\sqrt{7}$
${}^3_2F \rightarrow {}^3_2F$	$-\sqrt{(22)}/3\sqrt{7}$	${}^2_5S \rightarrow {}^2_5G$	$2\sqrt{(2)}/\sqrt{21}$
${}^3_2G \rightarrow {}^3_2G$	$-\sqrt{(11)}/3\sqrt{5}$	${}^2_5P \rightarrow {}^2_5F$	$3\sqrt{(7)}/14$
${}^3_2G \rightarrow {}^3_2G$	$4\sqrt{(33)}/3\sqrt{(35)}$	${}^2_5G \rightarrow {}^2_5G$	$\sqrt{(11)}/2\sqrt{7}$
${}^3_2H \rightarrow {}^3_2H$	$2\sqrt{(11)}/\sqrt{(13)}/3\sqrt{35}$		

TABLE V  
(Continued)

$2S+1\sqrt{L} \rightarrow$ $\rightarrow 2S'+1\sqrt{L}'$	$g$	$2S+1\sqrt{L} \rightarrow$ $\rightarrow 2S'+1\sqrt{L}'$	$g$
$n = 5$			
${}^2_1D \rightarrow {}^2_3D$	$-5/3 \sqrt{7}$	${}^2_3F \rightarrow {}^2_3F$	$-\sqrt{(11)/6}$
${}^2_3F \rightarrow {}^2_3F$	$-\sqrt{(10)/3}$	${}^2_3G \rightarrow {}^2_3G$	$\sqrt{(7)/2}$
${}^2_3G \rightarrow {}^2_3G$	$\sqrt{(22)/\sqrt{21}}$	${}^2_3I \rightarrow {}^2_3I$	$-\sqrt{(7)} \sqrt{(13)/6}$
${}^2_3H \rightarrow {}^2_3H$	$\sqrt{(22)/3}$	${}^2_5F \rightarrow {}^2_5F$	$\sqrt{(33)/2} \sqrt{7}$
${}^2_3D \rightarrow {}^2_5D$	$10 \sqrt{(2)/21}$	${}^2_5G \rightarrow {}^2_5G$	$-\sqrt{(11)} \sqrt{(13)/6} \sqrt{7}$
${}^2_5F \rightarrow {}^2_5F$	$-11 \sqrt{(2)/6} \sqrt{7}$	${}^2_5I \rightarrow {}^2_5I$	$-3 \sqrt{(39)/14}$
${}^2_5G \rightarrow {}^2_5G$	$3 \sqrt{(10)/14}$	${}^2_5H \rightarrow {}^2_5H$	$-\sqrt{(13)/2} \sqrt{21}$
${}^2_5I \rightarrow {}^2_5I$	$2 \sqrt{(7)} \sqrt{(13)/21}$	${}^2_3G \rightarrow {}^2_3H$	$-\sqrt{(7)} \sqrt{(13)/14}$
${}^2_5D \rightarrow {}^2_3F$	$-\sqrt{(35)/6}$	${}^2_3H \rightarrow {}^2_3I$	$-2 \sqrt{(13)/3}$
${}^2_3G \rightarrow {}^2_3G$	$-\sqrt{(11)/14} \sqrt{3}$		
${}^2_3H \rightarrow {}^2_3H$	$2 \sqrt{(11)/3} \sqrt{7}$		

are easily obtained from the corresponding  $2S+1\Gamma$  matrices of the  $d^3$ -system employing the principle of the electron-hole equivalence: with the diagonal elements the signs are reversed at the parameters  $D_s$  and  $D_t$ , and the expression  $-28B+14C$  is added to them.

Figs 1 and 2 show the courses of the terms of the  $d^3$ - and  $d^7$ -systems in an axial ligand field  $D_{\text{orb}}$  formed by two cyclopentadienyl rings (plots of  $E/B$  vs.  $D_t/B$  for different ratios  $D_s/D_t$  and  $C/B$ ). For practical reasons the diagrams are plotted for such ratios  $D_s/D_t$  and  $C/B$  as might occur in the sandwich complexes. Diagrams for other ratios of the parameters were reported elsewhere<sup>28</sup>.

## EXPERIMENTAL AND RESULTS

Vanadocene was prepared by reaction of vanadium tetrachloride with sodium cyclopentadienide in tetrahydrofuran<sup>29</sup>. The crude product was purified by two sublimations *in vacuo*. Prior to each spectral measurement the needed amount of vanadocene was resublimated. As vanadocene is sensitive to oxygen all manipulations with the pure sample were done under oxygen-free argon. Diethyl ether and n-pentane (for spectral measurements, Fluka AG.) were once distilled under an inert atmosphere. In the preparation of solutions for spectral measurements the solvent with a little  $\text{LiAlH}_4$  was distilled under an inert atmosphere direct to a weighed quantity of the sample in a closed, evacuated cell. The spectra were measured with a double-beam spectrophotometer Optica Milano, model CF 4 DR, at room temperature. The absorption spectrum of vanadocene was measured in n-pentane (region  $13000\text{--}43000\text{ cm}^{-1}$ ) and in diethyl ether ( $7700\text{--}15000\text{ cm}^{-1}$ ). The spectra were well reproducible throughout the two ranges of wave numbers. To be quite sure that the very weak absorption bands between  $7700$  and  $15000\text{ cm}^{-1}$  are not due to possibly present traces of the oxidation products of the sample, the latter was



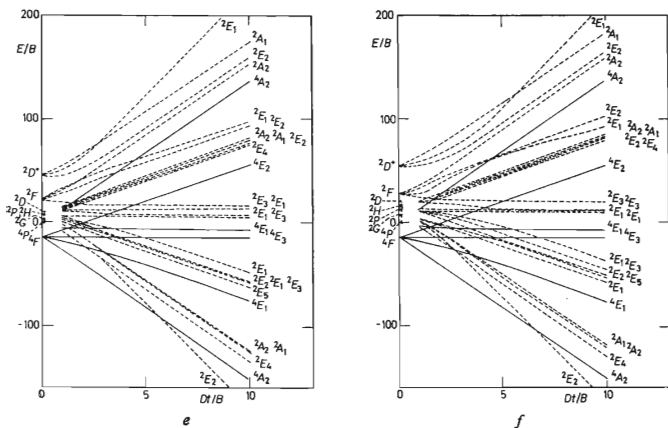


FIG. 1

The solid curves refer to quartet terms, the dashed curves to doublet terms. All the terms are of the  $g$ -type.  $a$ :  $Ds/Dt = 1$ ,  $C/B = 4.5$ ;  $b$ :  $Ds/Dt = 1.25$ ,  $C/B = 4.5$ ;  $c$ :  $Ds/Dt = 2$ ,  $C/B = 4.5$ ;  $d$ :  $Ds/Dt = 2$ ,  $C/B = 6$ ;  $e$ :  $Ds/Dt = 3$ ,  $C/B = 4.5$ ;  $f$ :  $Ds/Dt = 3$ ,  $C/B = 6$ .

oxidized after the spectrum had been measured and the spectral measurement was repeated. The original two weak bands of vanadocene completely vanished and no new bands were detected. The two bands were present even after repeated sublimation *in vacuo*. It can, therefore, be concluded that both bands (at 8955 and 13000  $\text{cm}^{-1}$ ) are due to absorptions by vanadocene itself, and not by some trace impurities or other admixtures. Fig. 3 shows the absorption spectrum of vanadocene in the region 13000—43000  $\text{cm}^{-1}$ , Fig. 4 the spectrum in the region 7700—15000  $\text{cm}^{-1}$ . The spectral characteristics of the electron absorption bands, obtained by the Gaussian analysis of the experimental curve between 7700 and 30000  $\text{cm}^{-1}$  (low-intensity part of the spectrum), are given in Table VII.

## DISCUSSION

A  $d^3$ -system in an axial field  $D_{\infty h}$  can theoretically have a high-spin ground state  $^4A_{2g}$  (whose orbital configuration, on disregarding the mixing due to the configuration interaction, is  $e_{2g}^2 a_{1g}^1$  at  $Ds/Dt > 1.25$  or  $a_{1g}^1 e_{2g}^2$  at  $Ds/Dt < 1.25$ ), or a low-spin ground state  $^2E_{2g}$  (the approximate orbital configuration is  $e_{2g}^3$ ), which can exist only at  $Ds/Dt > 1.25$ . The cross-section of ground state terms with different spin multiplicities correspond to such values of  $Ds$  and  $Dt$  as represent considerably strong

TABLE VI  
 A  $d^3$ -System in an Axial Ligand Field  $D_{\infty h}$ : the Weak Field Matrices

${}^4A_{2g}$ :	${}^4F$	$-\frac{3}{5}Ds - 6Dt - 15B$	${}^4P$	$\frac{3}{5}(3Ds + 5Dt)$
				$\frac{1}{3}Ds$
${}^4E_{1g}$ :	${}^4F$	$-\frac{3}{5}Ds - Dt - 15B$	${}^4P$	$\sqrt{6}(\frac{3}{5}Ds - Dt)$
				$-\frac{1}{3}Ds$
${}^4E_{2g}$ :	${}^4F$	$7Dt - 15B$		
${}^4E_{3g}$ :	${}^4F$	$Ds - 3Dt - 15B$		
${}^2E_{5g}$ :	${}^2H$	$-3Ds + 2Dt - 6B + 3C$		
${}^2E_{4g}$ :	${}^2H$	$-\frac{6}{5}Ds - 2Dt - 6B + 3C$	${}^2G$	$\frac{\sqrt{6}}{5}(-2Ds - 15Dt)$
				$-\frac{4}{3}Ds + Dt - 11B + 3C$
${}^2E_{3g}$ :	${}^2H$	$\frac{3}{5}Ds - 2Dt - 6B + 3C$	${}^2G$	$\frac{\sqrt{10}}{10}(-4Ds + 5Dt)$
				$-\frac{4}{3}Ds - \frac{2}{3}Dt - 11B + 3C$
${}^2A_{2g}$ :	${}^2H$	$2Ds + 2Dt - 6B + 3C$	${}^2P$	$-\frac{2}{7}\sqrt{5}Dt$
				$\frac{\sqrt{10}}{7}(2Ds + Dt)$
				$\frac{4}{3}Ds - Dt + 9B + 3C$
				$-\frac{4}{3}Ds - 6B + 3C$

${}^2A_{1g}$ :	$\frac{4}{7}Ds + \frac{9}{7}Dt - 11B + 3C$	$\frac{\sqrt{3}}{7}(2Ds - 20Dt)$	$\frac{\sqrt{7}}{7}(6Ds + 10Dt)$	$\frac{1}{3}D$	$\sqrt{(21)(\frac{3}{2}Ds + \frac{5}{2}Dt + 3B - 3Dt + 7B + 7C)}$
${}^2E_{2g}$ :	$\frac{5}{2}Ds - \frac{1}{3}Dt - 6B + 3C$	$\sqrt{(14)(-\frac{1}{3}Ds + \frac{2}{3}Dt)}$	$\sqrt{(10)(\frac{3}{2}Ds - \frac{1}{6}Dt)}$	$\frac{2}{3}F$	$-\frac{\sqrt{70}}{6}Dt$
	$\frac{8}{3}Ds - \frac{1}{14}Dt - 11B + 3C$	$\sqrt{(35)(\frac{8}{3}Ds + \frac{3}{14}Dt)}$	$\frac{7}{6}Dt + 9B + 3C$	$\frac{1}{7}(Ds + 18Dt)$	$-\frac{\sqrt{5}}{7}(Ds + 18Dt)$
				$\sqrt{(7)(-\frac{9}{2}Ds - \frac{3}{10}Dt)}$	$-\frac{1}{3}Ds + \frac{1}{4}\frac{9}{2}Dt + 3B + 3C$
				$\frac{7}{105}\frac{D}{Dt}$	$\frac{1}{7}\frac{\sqrt{30}}{Dt}$
				$\sqrt{(3)(-Ds - \frac{5}{2}Dt)}$	$\sqrt{(21)(-\frac{9}{2}Ds + \frac{4}{2}Dt + 3B) - Ds - \frac{1}{2}Dt + 7B + 7C}$
${}^2E_{1g}$ :	$\frac{9}{2}Ds + \frac{5}{2}Dt - 6B + 3C$	$-\frac{2}{3}Ds + \frac{2}{2}Dt$	$-\frac{2}{3}Ds + \frac{2}{2}Dt - 11B + 3C$	$\frac{2}{3}F$	$\frac{1}{7}(6Ds + \frac{10}{6}Dt)$
	$\frac{1}{3}Ds + \frac{9}{14}Dt - 11B + 3C$	$\frac{1}{7}(2Ds + \frac{9}{2}Dt)$	$\frac{3}{2}Ds - \frac{1}{6}Dt + 9B + 3C$	$\frac{1}{7}(2Ds + \frac{9}{2}Dt)$	$\sqrt{(70)(-\frac{9}{2}Ds + \frac{9}{2}Dt)}$
				$\frac{1}{14}Ds - \frac{1}{8}Dt + 9B + 3C$	$\frac{3}{14}Ds - \frac{3}{8}\frac{1}{14}Dt + 3B + 3C$
				$\frac{2}{3}D$	$\frac{2}{3}D$
				$\frac{\sqrt{210}}{3}Dt$	$-\frac{2}{3}\sqrt{(3)Dt}$
				$\frac{\sqrt{210}}{14}(2Ds + Dt)$	$-\frac{3}{2}\sqrt{3}Dt$
				$\sqrt{(30)(-\frac{1}{3}Ds + \frac{9}{2}Dt)}$	$\sqrt{(21)(\frac{8}{3}Ds - \frac{1}{14}Dt)}$
				$\sqrt{(21)(\frac{3}{4}Ds - \frac{2}{10}Dt + 3B)}$	$\frac{\sqrt{30}}{10}Ds$
				$\frac{1}{2}Ds + 2Dt + 7B + 7C$	$-\frac{3\sqrt{70}}{10}Ds$
					$\frac{2}{3}Ds - 6B + 3C$





it seems justified to assume that the ground state of dicyclopentadienyl  $d^3$ -complexes is the quartet state  ${}^4A_{2g}$ . This assumption is corroborated by the values of the magnetic moment, which in the investigated  $d^3$ -complexes (see above) are close to the spin-only values for three unpaired electrons in an orbitally non-degenerated ground state. Hence it can be concluded that in these  $d^3$ -complexes with the ground state  ${}^4A_{2g}[e_{2g}^2 a_{1g}^1]$  both one-electronic levels  $a_{1g}$  and  $e_{2g}$  exhibit a "high-spin" behaviour (whereas the third orbital, *i.e.* the energetically highest level  $e_{1g}$ , manifests a "low-spin" behaviour, because in the ground state of the complex this level is not occupied by any of the three  $d$ -electrons).

Knowledge of energies of the individual ligand-field states (terms) of a  $d^3$ -system in an axial field  $D_{\infty h}$  makes it possible to interpret the  $d-d$  transitions in the electronic spectra of sandwich  $d^3$  complexes. The long-wave region of the electronic spectrum of a metallocene complex contains  $d-d$  bands corresponding to both the spin-allowed one-electron transitions and some of the low-energy spin-forbidden transitions. In  $d^3$ -metallocenes with the ground state  ${}^4A_{2g}$  altogether three spin-allowed one-electron transitions can be expected:  ${}^4E_{1g} \leftarrow {}^4A_{2g}$  (orbital excitation  $e_{1g} \leftarrow a_{1g}$ ),  ${}^4E_{3g} \leftarrow {}^4A_{2g}$  ( $e_{1g} \leftarrow e_{2g}$ ),  ${}^4E_{1g} \leftarrow {}^4A_{2g}$  ( $e_{1g} \leftarrow e_{2g}$ ). Of the two terms  ${}^4E_{1g}$  the one of lower energy will be designated as  ${}^4E_{1g}^-$ , the other as  ${}^4E_{1g}^+$ . (It is worth while to note that at  $Ds/Dt = 1.25$  the states  ${}^4E_{1g}^-$  ( $e_{2g}^2 e_{1g}^1$ ) and  ${}^4E_{3g}$  would be equienergetical). The lowest spin-allowed transition can be preceded by several spin-forbidden transitions; thus at  $Ds/Dt = 2$  and  $Dt/B = 5$  (Fig. 1c) it can be preceded by the four transitions

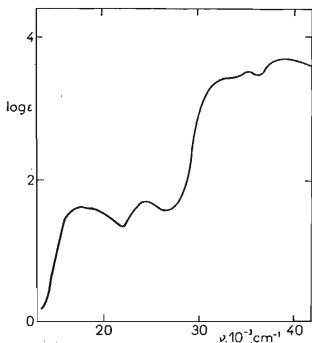


FIG. 3

Absorption Spectrum of Vanadocene in *n*-Pentane

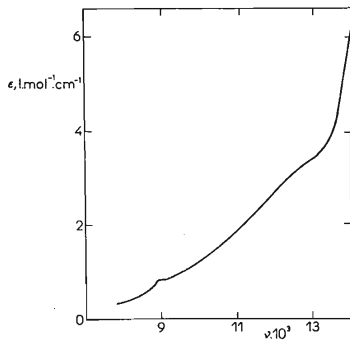


FIG. 4

Absorption Spectrum of Vanadocene in Diethyl Ether

${}^2E_{2g} \leftarrow {}^4A_{2g}$ ,  ${}^2E_{4g} \leftarrow {}^4A_{2g}$ ,  ${}^2A_{1g} \leftarrow {}^4A_{2g}$ ,  ${}^2A_{2g} \leftarrow {}^4A_{2g}$ , which might be detected in the spectrum. If, for example, the experimental energies of three spin-allowed and at least one spin-forbidden  $d-d$  transitions are known, it is possible to calculate all the four ligand-field parameters ( $Ds$ ,  $Dt$ ,  $B$ ,  $C$ ). This (simplified) ligand-field model will now be used to interpret the  $d-d$  transitions in the  $d^3$ -complexes studied.

*Vanadocene.* In the spectral region  $30\,000-40\,000\text{ cm}^{-1}$  vanadocene exhibits at least three absorption bands: at  $32\,000$ ,  $35\,400$  and  $39\,000\text{ cm}^{-1}$  (at the temperature of  $77^\circ\text{K}$  the wide band at  $39\,000\text{ cm}^{-1}$  splits into two bands<sup>4,6</sup>). Their molar absorptivities lie within the range  $2800-5000$ . This group of absorption bands, which will not be dealt with further, can in all probability be assigned to the intramolecular CT-transitions (ligand  $\leftarrow$  metal or metal  $\leftarrow$  ligand), intraligand transitions, or to the transition  $4p \leftarrow 3d$ .

In the spectral region  $7700$  to  $30\,000\text{ cm}^{-1}$ , which is the most important one for the ligand field problem, there have been found five absorption bands of low and very low intensities (Table III): two bands in the near IR region at  $8995\text{ cm}^{-1}$  (I) and  $13000\text{ cm}^{-1}$  (II), their molar absorptivities were below  $0.1$  and three bands in the visible region at  $17330\text{ cm}^{-1}$  (III),  $20240\text{ cm}^{-1}$  (IV) and  $24500\text{ cm}^{-1}$  (V), whose molar absorptivities were between  $20$  and  $50$ . As far as we know, bands I and II have not been previously observed. Bands III, IV and V, judging by their intensities and behaviour at lower temperatures<sup>4,6</sup>, can be assigned to the spin-allowed  $d-d$  transitions forbidden by Laport's rule. The intensities and oscillator strengths of bands I and II are much smaller than is usual for the spin-allowed transitions. Analogous bands of nickelocene have been assigned to the spin-forbidden transitions<sup>8</sup>. On the basis of the same considerations as accounted for the low-intensity bands in the electronic spectrum of nickelocene<sup>8</sup>, band II of vanadocene can be assigned to intercombination (spin-forbidden  $d-d$  transitions), stealing their intensity from normal  $d-d$  transitions through the spin-orbit coupling. The spin-orbit coupling constant which would account, according to the perturbation theory, for the intensity of this band is  $\zeta_{V^{2+}} \sim 160\text{ cm}^{-1}$ , which value is quite reasonable ( $\zeta$  for the free ion is  $169\text{ cm}^{-1}$ ). In the case of band I the assignment is more difficult. This band does not seem to be associated with any  $d-d$  transition; it is probably due to a multi-quantum vibrational transition. This assignment is supported by the following facts: 1. the intensity of the band cannot be accounted for by the spin-orbital coupling by means of the perturbation formula<sup>30</sup> (the calculated value of the constant  $\zeta^{V^{2+}}$  is about  $2.5$  times higher than that of the free ion  $V^{2+}$ ); 2. the shape, position and intensity of this band are identical with the shape, position and intensity of that band of ferrocene ( $8925\text{ cm}^{-1}$   $\epsilon_{\text{max}} = 0.13$ ) which can be assigned to the second overtone of the fundamental of ferrocene,  $3100\text{ cm}^{-1}$  (the same fundamental has been found even in the IR spectrum of vanadocene); 3. the oscillator strength of the absorption band is comparable with the value that might be expected for the second overtone of the given fundamental vibration.

According to the theory the spectrum of vanadocene (ground state  $^4A_{2g}$ ) should not contain more than three bands associated with one-electron  $d-d$  transitions. The four (possibly five) bands of vanadocene (three normal and one or two intercombination bands) must now be assigned to specified ligand field transitions; the splitting parameters  $D_s$ ,  $D_t$  and Racah's parameters  $B$ ,  $C$  will be calculated from the experimentally determined transition energies. Since the mode of assignment of the normal bands and the calculation of the parameters  $D_s$ ,  $D_t$  and  $B$  were essentially identical with the procedure employed with nickelocene<sup>8</sup> it would be needless to describe it in detail. Of all the assignments considered only one has proved justified (Table VII). According to this assignment bands III, IV and V can safely be ascribed to three one-electron quartet  $\leftarrow$  quartet transitions and band II, in all probability, to a doublet  $\leftarrow$  quartet transition. Employing the experimental energies of bands III, IV and V we calculated the parameters  $D_s$ ,  $D_t$  and  $B$  (Table X). The calculation of the remaining parameter  $C$  is difficult because band II cannot be assigned unequivocally to a definite transition. The terms diagram in Fig. 1c (which best fits the experimentally determined ratio  $D_s/D_t = 1.86$ ), for the experimental value  $D_t/B = 4.8$ , shows that the lowest excited quartet terms  $^4E_{1g}$ , is preceded by four doublet states ( $^2E_{2g}$ ,  $^2E_{4g}$ ,  $^2A_{2g}$ ,  $^2A_{1g}$ ) whose energies are generally dependent on four parameters, *i.e.* even on the parameter  $C$ . For this reason we have attempted assignment of band II (and possibly of band I, whose electronic nature has already been said to be highly questionable) by calculating the energies of transitions from the ground quartet state to the above-mentioned four doublet states employing the values of  $D_s$ ,  $D_t$  and  $B$ , calculated from the normal transitions, and chosen values of  $C$  (*i.e.* for different ratios of Racah parameters  $C/B$ ). The calculation is given in Table VIII. Of the four given assignments, for different ratios  $C/B$ , assignment *a*) can be ruled out since none of the doublet  $\leftarrow$   $\leftarrow$  quartet transition energies agrees with the experimental value for band II. The

TABLE VII  
Absorption Bands of Vanadocene ( $7\ 700\text{--}30\ 000\ \text{cm}^{-1}$ )

Band	$\nu_{\max}$ $\text{cm}^{-1}$	$\epsilon_{\max}$ $\text{l mol}^{-1}\ \text{cm}^{-1}$	Oscillator strength	Assignment
I	8 955	0.086	$3.26 \cdot 10^{-8}$	2nd overtone ( $3 \times 3\ 000\ \text{cm}^{-1}$ )
II	13 000	0.06	$4.79 \cdot 10^{-8}$	$d-d$ transition (intercombination)
III	17 330	41.8	$7.38 \cdot 10^{-4}$	$d-d$ transition $^4E_{1g}^- \leftarrow ^4A_{2g}$
IV	20 240	23.8	$2.78 \cdot 10^{-4}$	$d-d$ transition $^4E_{3g}^- \leftarrow ^4A_{2g}$
V	24 500	49.3	$8.85 \cdot 10^{-4}$	$d-d$ transition $^4E_{1g}^+ \leftarrow ^4A_{2g}$

TABLE VIII

Calculated Energies of the Lowest Spin-Forbidden Transitions of Vanadocene

Values employed for the calculation:  $D_s = 3\,756\text{ cm}^{-1}$ ,  $D_t = 2\,018\text{ cm}^{-1}$ ,  $B = 418\text{ cm}^{-1}$ .

$C$ $\text{cm}^{-1}$	$C/B$	Calculated energies, $\text{cm}^{-1}$		
		${}^2E_{4g} \leftarrow {}^4A_{2g}$	${}^2E_{2g}^{(1)} \leftarrow {}^4A_{2g}$	${}^2A_{2g} \leftarrow {}^4A_{2g}$
1 672	4	6 795	9 027	9 944
2 424	5.8	9 050	11 300	12 200
2 968	7.1	10 683	12 940	13 832
3 720	8.9	12 940	15 205	16 088

other assignments are principally possible unless there is a restricting condition of a maximum possible value of the ratio  $C/B$ . If there is not such a condition band II cannot be ascribed with certainty to one of the three possible doublet  $\leftarrow$  quartet transitions, according to assignment *b*) band I might correspond to the  ${}^2E_{4g} \leftarrow {}^4A_{2g}$  transition. This possibility cannot be ruled out because this intercombination band might accidentally have the same energy as the second overtone of the fundamental vibration. As for the ratio  $C/B$ , whose different values correspond to different possible assignments of band II, its upper limit in metallocene complexes is still a problem to be solved. The question is whether in complexes of this type the ratio  $C/B$  can be substantially higher than the free-ion value, *i.e.*  $\sim 4$ . Some authors (*e.g.*<sup>4</sup>) do not concede the possibility of a significant increase of the ratio  $C/B$  and assume that  $3 < C/B < 5$ , so that the value of this ratio remains close to that of the free ion. However, analysis of the  $d-d$  transitions of certain metallocenes reveals that in the given approximation of the ligand field theory a considerable increase in  $C/B$  really occurs (the ratio  $C/B$  for ferrocene is 8.8, whereas for the free ion it is 4.4; the value for nickelocene is 6.8, and 4.7 for the free ion). From the assignment of band II of vanadocene it follows that even in this metallocene the ratio  $C/B$  should increase from 4.3 to a minimum of 5.8. Until the question of the ratio  $C/B$  is solved it is impossible to put a limit to its value and an unequivocal assignment of band II is not yet possible. The problem of the ratio  $C/B$  in metallocene complexes will be the subject of a separate communication of this series. In the present paper we just want to point out that there exist some octahedral complexes<sup>31,32</sup> where the ratio  $C/B$  reaches values as high as 10.

*Chromicinium and its carborane analogues.* Since the carborane sandwich complexes have an approximate symmetry  $D_{5d}$  or  $D_{5h}$  (bis-dicarbolyde complexes), or  $C_{5v}$  (mixed cyclopentadienyl-dicarbolyde complexes), their ligand fields can be regarded<sup>33</sup> as approximately axial, *i.e.*  $D_{\infty h}$  or  $C_{\infty v}$ .

TABLE VIII  
(Continued)

Calculated energies, $\text{cm}^{-1}$		Assignment
${}^2A_{1g} \leftarrow {}^4A_{2g}$	${}^2E_{2g}^{(2)} \leftarrow {}^4A_{2g}$	
9 489	15 362	(a): band I $\sim {}^2E_{2g}^{(1)} \leftarrow {}^4A_{2g}$
12 870	18 650	(b): band II $\sim {}^2A_{1g} \leftarrow {}^4A_{2g}$ , band I $\sim {}^2E_{4g} \leftarrow {}^4A_{2g}$
15 265	20 962	(c): band II $\sim {}^2E_{2g}^{(1)} \leftarrow {}^4A_{2g}$
18 509	24 077	(d): band II $\sim {}^2E_{4g} \leftarrow {}^4A_{2g}$

In their long-wave regions<sup>11,15</sup> the electronic spectra of  $[\text{Cr}(\text{C}_5\text{H}_5)_2]^+$  and  $[\text{Cr}(\text{Cb})_2]^{2-}$ , where  $\text{Cb} = [(3)\text{-}1,7\text{-B}_9\text{C}_2\text{H}_{11}]^{2-}$ , are similar to that of vanadocene. The region  $17000\text{--}27000\text{ cm}^{-1}$  contains three low-intensity bands, which can be considered to be the normal  $d\text{-}d$  bands (the high-intensity bands in the short-wave region are of a different electronic nature, so that they are irrelevant to the ligand field problem). These absorption bands can be assigned to the three spin-allowed one-electron  $d\text{-}d$  transitions, as is shown in Table IX. Employing the energies of thus assigned  $d\text{-}d$  transitions it is again possible to calculate the splitting parameters  $D_s$ ,  $D_t$  and Racah parameter  $B$  from the corresponding quartet energy matrices (Table X).

The absorption curve of  $[\text{Cr}(\text{C}_5\text{H}_5)_2]\text{I}$ , measured by Fischer and Ulm<sup>13</sup>, has an inflexion at  $25000\text{ cm}^{-1}$ , whose origin is not clear; it cannot be assigned to the  $d\text{-}d$  transition  ${}^4E_{1g}^+ \leftarrow {}^4A_{2g}$  (instead of the band at  $27030\text{ cm}^{-1}$ ) because the value of the parameter  $B$  would be too low. With the given spectral data the experimental value

TABLE IX  
 $d\text{-}d$  Bands of the Sandwich Complexes of Cr(III)

$[\text{Cr}(\text{C}_5\text{H}_5)_2]^+$			$[\text{Cr}(1,7\text{-B}_9\text{C}_2\text{H}_{11})_2]^{2-}$			$d\text{-}d$ Transition
$\lambda_{\text{max}}$ nm	$\nu_{\text{max}}$ $\text{cm}^{-1}$	$\epsilon_{\text{max}}$ $\text{l mol}^{-1}\text{ cm}^{-1}$	$\lambda_{\text{max}}$ nm	$\nu_{\text{max}}$ $\text{cm}^{-1}$	$\epsilon_{\text{max}}$ $\text{l mol}^{-1}\text{ cm}^{-1}$	
370	27 030	630	379	26 380	1 500	${}^4E_{1g}^+ \leftarrow {}^4A_{2g}$
455	21 980	210	470	21 280	250	${}^4E_{3g} \leftarrow {}^4A_{2g}$
560	17 860	270	520	19 230	230	${}^4E_{1g}^- \leftarrow {}^4A_{2g}$

of the parameter  $C$  can be determined in neither of the two complexes of Cr(III). To determine the parameter  $C$  it would be necessary, in the given approximation, to know the energy of at least one of the spin-forbidden doublet  $\leftarrow$  quartet transitions, which, however, are not present in the spectra investigated. Since the available spectral data are very incomplete it will be necessary to study the long-wave spectra of these complexes in detail.

Since we already know the experimental values of  $D_s$ ,  $D_t$  and  $B$  (Table X) for two ligand systems (the bis-cyclopentadienyl and bis-dicarbolyde systems) of the Cr(III)-complex, it is possible to calculate<sup>22</sup> the parameters for the mixed complex  $C_5H_5 \cdot CrCb$  and, from these, the energies of the three one-electron quartet  $\leftarrow$  quartet  $d-d$  transitions, or the positions of the corresponding bands. The agreement between the calculated and the experimental values is satisfactory (Table XI). The bands  ${}^4E_1^- \leftarrow {}^4A_2$ , not reported in the spectrum of the mixed complex<sup>15</sup>, should occur at 540 nm.

### The Bonding in the $d^3$ -Complexes of V(II) and Cr(III)

Employing the determined values of  $D_s$  and  $D_t$  we calculated the energy differences between the individual split  $d$ -levels of V(II) and/or Cr(III) for all the  $d^3$ -sandwich complexes studied (Table X). From these differences it follows that the order of the  $d$ -orbitals is always  $e_{1g} > a_{1g} > e_{2g}$ , the difference  $e_{1g} - a_{1g}$  being considerably higher than  $a_{1g} - e_{2g}$ . This order, derived from analysis of the electronic spectra, is identical with that found in the semiempirical MO procedure<sup>3,4</sup>. The wave function of the ground state  ${}^4A_{2g}$  is composed of the wave functions of the states  ${}^4A_{2g}(F)$ :  $:e_{2g}^2 a_{1g}^1$  and  ${}^4A_{2g}(P)/a_{1g}^1 e_{1g}^2$ . Thus with vanadocene the ground state wave function

TABLE X

Ligand Field Parameters and Bonding Parameters of Vanadocene and Sandwich Complexes of Cr(III)

Parameter	V(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	Cr(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> <sup>+</sup>	C <sub>5</sub> H <sub>5</sub> Cr (1,7-B <sub>9</sub> C <sub>2</sub> H <sub>11</sub> )	[Cr(1,7-B <sub>9</sub> C <sub>2</sub> H <sub>11</sub> ) <sub>2</sub> ] <sup>-</sup>
$D_s, \text{cm}^{-1}$	3 756	4 299	4 028	3 758
$D_t, \text{cm}^{-1}$	2 018	2 087	2 165	2 245
$B, \text{cm}^{-1}$	418	513	486	457
$\beta$	0.55	0.56	0.53	0.50
$E(e_{1g}) - E(a_{1g}), \text{cm}^{-1}$	16 424	16 569	17 622	18 692
$E(a_{1g}) - E(e_{2g}), \text{cm}^{-1}$	4 934	6 763	5 287	3 807
$f(M-C_5H_5), \text{mdyn}/\text{\AA}^a$	1.5	—	—	—
$\gamma_{CH}, \text{cm}^{-1} \text{\AA}^a$	783	—	—	—

<sup>a</sup> Values taken from Fritz's paper<sup>33</sup>.

is 84% the *F*-state function and 16% the *P*-state function; with chromicinium it is 85% *F* and 15% *P*. Consequently, in an approximation neglecting the configuration interaction the ground state is  ${}^4A_{2g}(F)$  with the corresponding orbital configuration.

The nephelauxetic parameter  $\beta$  for V(II) in vanadocene is 0.55 ( $B_{ion} = 775 \text{ cm}^{-1}$ , ref.<sup>34</sup>), for Cr(III) in the dicyclopentadienyl and the bis-dicarbollide complexes it equals 0.56 and 0.50, respectively ( $B_{ion} = 918 \text{ cm}^{-1}$ , ref.<sup>34</sup>). Comparison of the determined values of the parameters for the two cyclopentadienyl  $d^3$ -systems,  $V(C_5H_5)_2$  and  $[Cr(C_5H_5)_2]^+$ , suggests that the nature of bonds in these two complexes is approximately the same. As the parameter  $\beta$  is a measure of covalency of the bond between the central atom and the ligand it is of interest to compare its values for vanadocene and chromicinium with those reported for ferrocene and nickelocene<sup>8</sup>. From its value in all metallocenes ( $\beta \approx 0.4-0.6$ ) it can be judged that the metal-cyclopentadienyl bond is rather covalent. Comparison of the individual  $\beta$  values indicates that the bond  $Fe-C_5H_5$  is more covalent than any of the bonds  $M-C_5H_5$ , where  $M = V, Cr, Ni$ . This conclusion accords with the magnitude of the force constants of the bonds  $M-C_5H_5$  ( $Fe(II) > V(II) > Ni(II)$ ) and with the frequencies of the IR-active vibration  $\gamma_{CH}$ , which is an empirical criterion of covalency of the bond  $M-C_5H_5$  (ferrocene  $>$  vanadocene  $>$  nickelocene)<sup>35</sup>.

On the basis of the determined values<sup>7,8</sup> of  $D_s$ ,  $D_t$  and  $\beta$  the central atoms of the compared dicyclopentadienyl complexes can be arranged into a spectrochemical series,  $Fe(II) > Cr(III) > V(II) > Ni(II)$ , and a nephelauxetic series,  $Ni(II) \approx Cr(III) \geq V(II) > Fe(II)$ .

If further research succeeds in extending these series to include other central atoms it will be interesting to compare them with the series known for complexes of other types, e.g. the complexes of cubic symmetry.

The results obtained by analysis of the  $d-d$  spectra of the two sandwich complexes of Cr(III) yield also some information on the dicarbollide ligand and make possible its comparison with cyclopentadienyl: 1. The parameters  $D_s$  and  $D_t$  of the dicarbollide ligand, being a binegative anion, are comparable and even about 15% lower than the parameters of the cyclopentadienyl ligand, the mononegative anion. Hence

TABLE XI

Calculated and Found  $d-d$  Transitions of the Complex  $[Cr(C_5H_5)(B_9C_2H_{11})]^-$ 

$d-d$ Transition	$\nu_{max} \text{ cm}^{-1}, \lambda_{max} \text{ nm}$			
	calculated		found	
${}^4E_1^+ \leftarrow {}^4A_2$	26 674	375	26 250	381
${}^4E_3 \leftarrow {}^4A_2$	21 620	463	23 470	426
${}^4E_1^- \leftarrow {}^4A_2$	18 570	539	?	?

it can be judged that the active "sandwich" part of dicarbollide (*i.e.* the open face  $B_3C_2H_5$ ) carries approximately the same charge as cyclopentadienyl, *i.e.* one negative charge. The other negative charge is obviously located in the "non-sandwich" part of the ligand, *i.e.* in the lower part of the carborane "pot". 2. The nephelauxetic parameter shows that the bond Cr-ring in the dicarbollide complex is more covalent than in the cyclopentadienyl complex. This fact accords with the difference in the chemical stability of the two complexes (chromocinium is very labile<sup>13</sup>, the carborane complex is stable<sup>15</sup>). 3. Comparison of the parameters  $D_s$  and  $D_t$  reveals that the ratio  $D_s/D_t$  is greater with  $C_5H_5^-$  than with  $Cb^{2-}$  (the values of the two parameters change inversely, if  $D_t$  increases  $D_s$  decreases and *vice versa*).

### $d^7$ -Systems

A  $d^7$ -system in an axial field of two sandwich ligands can theoretically have a high-spin (quartet) or a low-spin (doublet) ground state. The cross-section of the terms of ground states with different multiplicities  ${}^4A_{2g}$  (approximate orbital configuration  $e_{2g}^4 a_{1g}^1 e_{1g}^2$ ) and  ${}^2E_{1g}$  ( $e_{2g}^4 a_{1g}^2 e_{1g}^1$ ) occurs at such values of  $D_s$  and  $D_t$  as correspond to a weak ligand field (if  $B_{\text{complex}} \approx 500 \text{ cm}^{-1}$ , which would be a reasonably possible value for *e.g.*, Co(II) in cobaltocene, then for  $D_s/D_t = 2$  the cross-section would correspond to  $D_s \approx 2700 \text{ cm}^{-1}$ ,  $D_t \approx 1350 \text{ cm}^{-1}$ ; for a metallocene these values are too low). The present-day knowledge suggests that dicyclopentadienyl  $d^7$ -complexes should represent "strong fields" having low-spin ground states. The magnetic momenta of the  $d^7$  metallocenes thus far known prove this expectation to be correct (Co( $C_5H_5$ )<sub>2</sub>:  $\mu_{\text{eff}} = 1.76 \pm 0.07 \mu_B$ ; Ni( $C_5H_5$ )<sub>2</sub><sup>+</sup>:  $\mu_{\text{eff}} = 1.82 \pm 0.09 \mu_B$ , ref.<sup>36</sup>). On the basis of EPR measurements<sup>37</sup> it has been postulated that cobaltocene has both a spin and an orbital doublet, *i.e.* the ground state  ${}^2E_{1g}$ . It should be noted that no high-spin sandwich  $d^7$ -complex has as yet been found. Consequently, the one-electron  $d$ -levels exhibit in this case a "low-spin behaviour". For the sake of comparison it should also be mentioned that the ground state of cobaltocene  ${}^2E_{1g}(e_{2g}^4 a_{1g}^2 e_{1g}^1)$  was determined even by a semiempirical MO-calculation<sup>5</sup>.

Knowledge of the ligand field states of a  $d^7$ -system might be used to interpret the  $d-d$  transitions in electronic spectra. A complex with the ground state  ${}^2E_{1g}$  has altogether eight monoexcited doublet states

$$\begin{aligned} e_{1g} \leftarrow a_{1g} : & {}^2A_{1g}, {}^2A_{2g}, {}^2E_{2g} \\ e_{1g} \leftarrow e_{2g} : & {}^2E_{2g}, {}^2E_{2g}, {}^2A_{1g}, {}^2E_{4g}, {}^2A_{2g}, \end{aligned}$$

so that there can occur as many as eight one-electron doublet  $\leftarrow$  doublet transitions from the ground state  ${}^2E_{1g}$ . These transitions, forbidden by Laporte's rule, might gain their intensity by the vibronic coupling with the skeletal vibrations of a metallocene ( $a_{1u}, a_{2u}, e_{1u}, e_{2u}$ ). Since the electronic spectrum has not yet been thoroughly in-



investigated in any  $d^7$ -metallocene complex it is at present impossible to use our theoretical results on the ligand field for dealing with this problem.

## REFERENCES

1. Šustorovič E. M., Djatkina M. E.: Dokl. Akad. Nauk SSSR 133, 141 (1960).
2. Šustorovič E. M., Djatkina M. E.: Ž. Neorgan. Chim. 6, 1247 (1961).
3. Schachtschneider J. H., Prins R., Ros P.: Inorg. Chim. Acta 1, 462 (1967).
4. Prins R.: Thesis. University of Amsterdam, 1967.
5. Rettig M. F., Drago R. S.: J. Am. Chem. Soc. 91, 3432 (1969).
6. Prins R., van Voorst J. D. W.: J. Chem. Phys. 49, 4665 (1968).
7. Scott D. R., Becker R. S.: J. Organometal. Chem. 4, 409 (1965).
8. Pavlík I., Černý V., Maxová E.: This Journal 35, 3045 (1970).
9. Fischer E. D., Hafner W.: Z. Naturforsch. 9b, 503 (1954).
10. Weiss E., Fischer E. O.: Z. Anorg. Allgem. Chem. 278, 219 (1955).
11. Prins R., Biloen P., van Voorst J. D. W.: J. Chem. Phys. 46, 1216 (1967).
12. de Liefde Meijer H. J., Janssen M. J., van der Kerk G. J. M.: Rec. Trav. Chim. 80, 831 (1961).
13. Fischer E. O., Ulm K.: Chem. Ber. 95, 692 (1962).
14. Hawthorne M. F.: J. Am. Chem. Soc. 90, 879 (1968).
15. Ruhle H. W., Hawthorne M. F.: Inorg. Chem. 7, 2279 (1968).
16. Robertson R. E., McConnell H. M.: J. Phys. Chem. 64, 70 (1960).
17. Piper F. S., Carlin R. L.: J. Chem. Phys. 33, 1208 (1960).
18. Griffith J. S.: *The Theory of Transition-Metal Ions*. Cambridge Univ. Press, Cambridge 1964.
19. Griffith J. S.: *The Irreducible Tensor Method for Molecular Symmetry Groups*. Prentice-Hall International, London 1962.
20. Heine V.: *Group Theory in Quantum Mechanics*. Pergamon Press, London 1964.
21. *Tables of Clebsch-Gordan Coefficients*. Science Press, Peking 1965.
22. Schläfer H. L., Gliemann G.: *Einführung in die Ligandenfeldtheorie*. Geest & Porting, Leipzig 1967.
23. Condon E. U., Shortley G. H.: *The Theory of Atomic Spectra*. Cambridge Univ. Press, Cambridge 1964.
24. Fieschi R., Löwdin P. O.: *Atomic State Wave Functions Generated by Projection Operators*. Technical Note 4. Uppsala 1957.
25. Fano U., Racah G.: *Irreducible Tensorial Sets*. Academic Press, New York 1959.
26. Rotenberg M., Bivins R., Metropolis N., Wooten J. K.: *The 3-j and 6-j Symbols*. The Technology Press, Massachusetts Institute of Technology, 1959.
27. Slater J. C.: *Quantum Theory of Atomic Structure*, Vol. II. McGraw-Hill, New York 1960.
28. *Archives of the Department of General and Inorganic Chemistry*. Institute of Chemical Technology, Pardubice.
29. Fischer E. O., Vigourex S.: Chem. Ber. 91, 2205 (1958).
30. McGlynn S. P., Smith J. K.: J. Mol. Spectry 6, 164 (1961).
31. Liehr A. D.: J. Phys. Chem. 67, 1314 (1963).
32. Lever A. B. P.: Advan. Chem. Ser. 62, 430 (1967).
33. Scott D. R.: J. Organometal. Chem. 6, 429 (1966).
34. Tanabe Y., Sugano S.: J. Phys. Soc. Jap. 9, 766 (1954).
35. Fritz H. P.: Chem. Ber. 92, 780 (1959).
36. Engelmann F.: Z. Naturforsch. 8b, 775 (1953).
37. Nussbaum M., Voigtländer J.: Z. Naturforsch. 20a, 1417 (1965).

Translated by J. Salák.