

LIGAND FIELD THEORY, $d-d$ SPECTRA OF FERROCENE AND OTHER d^6 -METALLOCENES*

V. ČERNÝ, I. PAVLÍK and E. KŮSTKOVÁ-MAXOVÁ

*Department of General and Inorganic Chemistry,
Institute of Chemical Technology, 532 10 Pardubice*

Received September 8th, 1975

Dedicated to Professor S. Škramovský on the occasion of his 75th birthday.

The approximation of weak and strong ligand field of $D_{\infty h}$ symmetry neglecting the spin-orbit coupling has been used for calculation of the LF-level energies for d^6 -metallocenes. The values obtained have been used for a detailed interpretation of $d-d$ spectrum of ferrocene and of $d-d$ spectra of biscyclopentadienyl complexes of Ru(II) and Co(III), biscarborane and mixed cyclopentadienyl-carbone sandwiches of Fe(II) and Co(III). The intensive long-wave absorption bands of biscarborane Ni(IV)-complexes are of CT-nature. LF-Parameters (D_s , D_t , B , resp. C) and nephelauxetic ratio have been determined for the individual complexes. The nature of the nephelauxetic effect and chemical properties of the both sandwich-cp and cb-ligands is discussed.

Long-wave part of electronic spectra of some metallocenes contains low-intensity $d-d$ bands which can be interpreted using the ligand field theory. If the experimental assigned $d-d$ energies are used as the input data for theoretical energies of quantum LF-transitions, splitting and electronic repulsion parameters can be calculated which give (either directly or after further analysis) information about the details of bonding relations. Such a procedure proved successful with d^3 - and d^8 metallocenes¹⁻⁶. The same procedure is used for d^6 -metallocenes Fe cp₂, Ru cp₂, [Co cp₂]⁺, [Fe cb₂]²⁻, [Co cb₂]⁻, Ni cb₂, [Fe cp cb]⁻, and Co cp cb (cp and cb are cyclopentadienyl (C₅H₅⁻) and carborane (1,2-C₂B₉H₁₁⁻) anions, respectively).

All the given d^6 -metallocenes are diamagnetic^{7,8}. The biscyclopentadienyl complexes are stable to oxidation. In the case of the biscarborane complexes the redox stability depends on the oxidation number of the central ion: the complex [Fe^{II} cb₂]²⁻, *i.e.* the carborane analogue of ferrocene, is extremely sensitive to oxidation, the complex [Co^{III} cb₂]⁻ is stable to oxidation and Ni^{IV} cb₂ itself is an oxidizing agent. The both sandwich ligands cp and cb differ in their ability to stabilize or destabilize the given oxidation state of the central ion: cp stabilizes low oxidation states, whereas cb stabilizes the higher ones.

The electronic spectrum of d^6 -metallocenes measured at 300 K consists of two $d-d$ bands, although the LF-theory predicts overall three spin-allowed $d-d$ transitions (one-electron). The apparent discrepancy was elucidated first by measuring the spectra at 77 and 4.2 K (ferrocene⁹⁻¹¹, ruthenocene and cobalticenium¹¹), which showed that the $d-d$ spectrum is, in fact, formed by three spin-allowed bands (at sufficient resolution).

* Part XX in the series On the Chemistry of "Sandwich" Complexes; Part XIX see ref.⁶.

So far only the incomplete strong field LF-matrices (limited configuration interaction, *viz* between the mono-excited states)^{11-13,15-17} were used for interpretation of the *d-d* absorption bands of *d*⁶-metallocenes. In the present work complete LF-matrices (neglecting spin-orbital interactions) have been used for detailed interpretation of the *d-d* spectrum of ferrocene with the aim of determination of the differences between the parameter values obtained by "complete" and "limited" LF-theory, *i.e.* with the aim to judge whether the use of the "limited" LF-theory is justified.

THEORETICAL

The ligand field of the *d*^{*n*}-complexes of M cp₂ type possesses axial symmetry^{3,18,19}, whereas those of M cb₂ and M cpcb complexes are approximatively axial¹⁵ (M cp₂ and M cb₂: *D*_{∞h}, M cb cn: *C*_{∞v}).

The many-electron problem (*d*⁶-ion in axial *D*_{∞h} field with positive values of parameters of the ligand field strength *D*_s and *D*_t^{1,3,20}) was solved in the weak and strong field approximation neglecting the spin-orbit coupling (for the weak field by the Racah method of irreducible tensor operators¹, for the strong field by calculation with computer using the program²¹). For the complete set of matrices of the strong and weak fields see²²; it is available on request.

Dependence of the energy of individual LF-states on the LF-parameters *B*, *C*, *D*_s, and *D*_t was determined for the parameters ratios *C/B* = 4.5, 6, 7.5, 9 and *D*_s/*D*_t = 1, 1.25, 1.5, 1.75, 2, 3, 4. Three of the diagrams obtained are given in Fig. 1.

From the analysis of all the energy diagrams obtained it follows that there are overall four theoretical possibilities of assignment of three energetically lowest spin-allowed *d-d* transitions (from the ground state ¹*A*_{1g}):

$${}^1E_{3g} < {}^1_aE_{1g} < {}^1_bE_{1g} \quad (\text{for } D_s/D_t < 1.5), \quad (1)$$

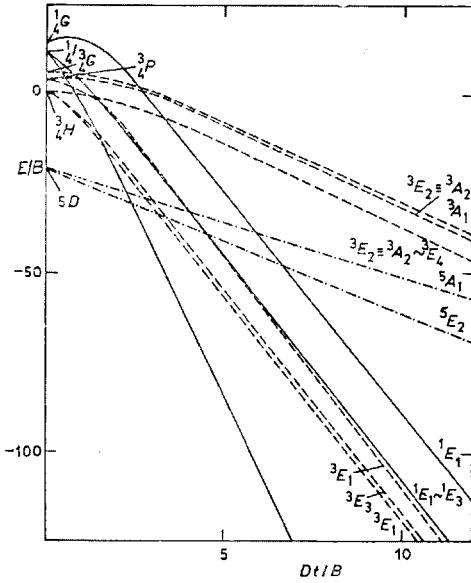
$${}^1_aE_{1g} < {}^1E_{3g} < {}^1_bE_{1g}, \quad (2)$$

$${}^1_aE_{1g} < {}^1E_{2g} < {}^1E_{3g} \quad (\text{for } D_s/D_t \geq 4 \text{ and } D_t/B \leq 8), \quad (3)$$

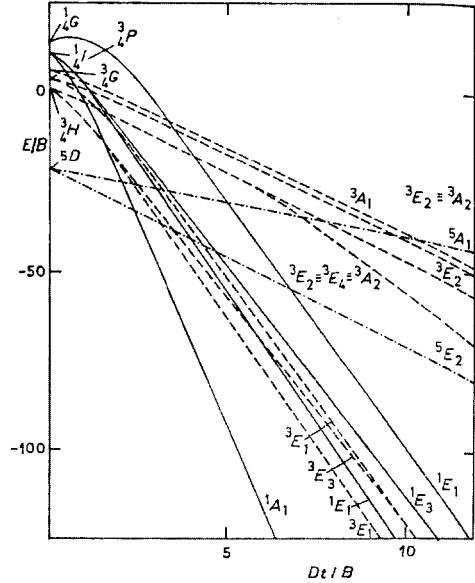
$${}^1_aE_{1g} < {}^1E_{2g} < -E_{1g} \quad (\text{for } D_s/D_t \geq 4 \text{ and } D_t/B \geq 8). \quad (4)$$

The lowest triplet level is ³*aE*_{1g}, being followed by the levels ³*E*_{3g} and ³*bE*_{1g} (the first two triplet states are almost equienergetical for small *D*_s/*D*_t values). At certain LF-parameter values some of the levels ³*A*_{2g}, ⁵*E*_{2g} or ⁵*A*_{1g} are also involved.

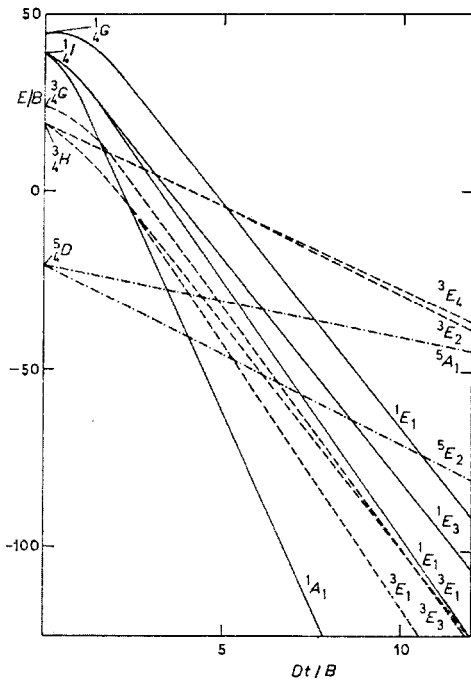
As the matrix ¹*A*_{1g} (involving the ground state) and the matrices ¹*E*_{1g}, ¹*E*_{3g} (involving all mono-excited states) are of high order, it is impossible to determine the LF-parameters after introducing the experimental excitation energies by the methods which had proved successful with other *d*^{*n*}-metallocenes^{1,3}. It is also not



a



b



c

FIG. 1

Dependence of Energy (in B Units) on Dt/B in the Case of d^6 -Electron System in the Field of Symmetry $D_{\infty h}$

All the terms are of the g -type. Only the terms with the smallest energy values are given in the pictures. — singlets, - - - triplets, - · - · - quintets a : $Ds/Dt = 1.5$, $C/B = 4.5$; b : $Ds/Dt = 2$, $C/B = 4.5$; c : $Ds/Dt = 2$, $C/B = 9$.

suitable to "facilitate" the solution by introducing *a priori* premisses concerning the relations between the individual parameters^{6,23-25}, especially the ratio C/B , because this procedure can bring about a disturbance of internal consistency of the LF-theory²⁴. Therefore, it was necessary to develop such a procedure which allows to determine the LF-parameters (D_s , D_t , B , C), without any *a priori* presumptions about their mutual relations, even from secular equations of high orders. In the given case use has been made of that the energies of the terms (E/B) change approximately linearly with the ratios D_t/B , C/B and D_s/B ($= D_t/B \cdot D_s/D_t$), beginning from the ratio $D_t/B \geq 2$. Coefficients of these ratios have been determined from the calculated energy values by the least squares method. The formulas reproducing approximately the dependence of energy levels on the LF-parameters were obtained by multiplication of the original formulas by the quantity B . Thus *e.g.* the following equation was obtained: $E(^1A_{1g}) = -8.91B + 7.42C - 3.94D_s - 15.70D_t$. From such relations the values of all four parameters were calculated after introducing experimental energies, and then they were introduced back into the complete secular equations. From the difference between the experimental and the new calculated energy values the corrections of LF-parameters were calculated. Their corrected values were again introduced into the secular equations. The iteration procedure was stopped when the difference between the calculated and the experimental energies of the $d-d$ transitions decreased below 200 cm^{-1} .

EXPERIMENTAL

Ferrocene was prepared by reaction²⁶ of cyclopentadiene with ferrous chloride in diethylamine. For spectral measurements the substance was sublimed *in vacuo* three times. Ruthenocene was prepared²⁷ by reaction of bis(2,4-pentandionato)ruthenium(III) complex with cyclopentadienylmagnesium bromide. The product was purified chromatographically²⁸ and then by vacuum sublimation. Cobalticinium salts were prepared by reaction²⁹ of tris(2,4-pentandionato)cobalt(III) complex with cyclopentadienylmagnesium bromide. The solutions containing cobalticinium cation were transformed into the respective hydroxide, chloride and bromide by means of ion exchangers. Reaction of aqueous cobalticinium solution with sodium tetrafluoroborate gave $[\text{Co}(\text{C}_5\text{H}_5)_2]\text{BF}_4$. Carborane complex of Fe(II), $\text{Cs}_2[\text{Fe}(1,2\text{-C}_2\text{-B}_9\text{H}_{11})_2]$, was obtained by reduction of the complex $\text{Cs}[\text{Fe}^{\text{III}}\text{cb}_2]$ by sodium amalgam in aqueous acetone medium. The product was recrystallized from toluene-acetone mixture. Carborane complex of Co(III), $\text{Cs}[\text{Co}\text{cb}_2]$, was prepared by the hydroxide method³⁰, *i.e.* reaction of cesium salt of carborane anion with cobalt(II) hydroxide. The product was recrystallized from acetonitrile. Carborane complex of Ni(IV), Nicb_2 , was prepared³⁰ by oxidation of $\text{Rb}[\text{Ni}^{\text{III}}\text{cb}_2]$ with ferric chloride and was purified by crystallization from n-heptane and subsequent chromatography. Mixed cyclopentadienyl-carborane complex of Co(III), $\text{Co}^{\text{III}}\text{cp cb}$, was prepared in the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague-Řež.

The spectral measurements were carried out with the use of a double-beam spectrophotometer Optica (Milano) Model CF-4 DR. The apparatus was calibrated by the spectral lines of sodium, hydrogen and mercury. The measurements were carried out at 25°C . Ferrocene was measured in n-heptane, methanol, diethyl ether and acetonitrile, ruthenocene was measured in n-heptane.

TABLE I
Absorption Spectra of d^6 -Metallocenes

d^6 -Metallocene	$d-d$ Bands			
	ν , cm^{-1}	ϵ_{max}	ν , cm^{-1}	ϵ_{max}
Fe cp_2^a	22 800	95	30 700	48
Ru cp_2^a	31 100	218	36 250	194
Co cp_2^b	24 750	229	33 330	1 137
Fe cb_2^{2-c}	19 900	182	26 200	167
Co cb_2^d	22 500	460	28 500 sh	2 500
Fe cp cb^{-e}	21 050	219	27 950	268
Co cp cb^e	23 700	364	31 250 sh	545
Ni cb_2^f				

ϵ_{max} Molar absorptivity ($l \cdot \text{mol}^{-1} \text{cm}^{-1}$), sh shoulder; ^a in hexane; ^b chloride in water; ^c cesium salt in acetonitrile; ^d cesium salt in methanol; ^e taken from ref.³⁰; ^f in cyclohexane.

Cobalticinium salts (OH^- , Cl^- , Br^- , BF_4^-) were measured in water and ethanol. Spectra of the carborane compounds were measured in acetonitrile and methanol, the complex Ni cb_2 was measured in *n*-heptane and cyclohexane. All the spectra were measured in the range 210 to 1000 nm. The measured data are given in Table I. Our results agree with the spectral measurements of Fe cp_2 ^{11,12,16,31}, Ru cp_2 ^{11,32}, cobalticinium^{11,29}, cb -complexes⁸.

RESULTS AND DISCUSSION

In Theoretical it was shown that there are four different assignments of the three energetically lowest spin-allowed $d-d$ transitions. Out of them only two (denoted (1) and (2)) turned out to be real when confronted with experiment. The assignments (3) and (4) must be excluded, because they lead to non-realistic LF-parameters values B , C , D_s and D_t (ref.²²).

The assignment (1) results in the orbital order $a_{1g} < e_{2g}$, which was not discussed in the "incomplete" LF-theory. This assignment agrees with the *ab initio* SCF-LCAO-MO calculations of Veillard and coworkers^{33,34}, however, the order of the one-electron levels found by SCF-MO calculation can differ from that determined by LF-theory for fundamental reasons, as it was pointed out by Ballhausen and Gray³⁵ and, in the special case of ferrocene, by Hendrickson³⁶.

Although the arguments of Veillard and coworkers³⁴, concerning the temperature dependence of intensities of individual spin-allowed ferrocene bands, could be transferred to the assignment (1) by means of LF-theory, the arguments of Eyring and coworkers³⁷, concerning the explanation of magnetic circular dichroism (MCD) of ferrocene, cannot be used due to the lack of the explanation as to why are the

TABLE I
(Continued)

Charge-transfer and intraligand bands					
ν, cm^{-1}	ϵ_{max}	ν, cm^{-1}	ϵ_{max}	ν, cm^{-1}	ϵ_{max}
37 750	1 700	43 800	4 400	50 000	49 000
		47 600	5 700		
38 500	36 300				
32 900	2 230	37 000	5 910		
35 100	46 000				
		46 950	30 600		
36 650	33 600	48 100	54 000		
23 600	2 270	33 600	37 000		

both MCD-bands *Ia* (${}^1A_{1g} \rightarrow {}^1E_{3g}(a_{1g}^2 e_{2g}^3 e_{1g}^1)$) according to assignment (1) and *Ib* (${}^1A_{1g} \rightarrow {}^1E_{1g}(a_{1g}^2 e_{2g}^3 e_{1g}^1)$) negative. Next — according to the LF-theory for the assignment (1) it is characteristic that the lowest spin-forbidden bands are close to one another (see Fig. 1a), which could serve as experimental criterion of this assignment. However, this near degeneracy has not yet been experimentally proved. Thus all these reasons indicate that the assignment (1) is not justified, even though the calculated positions of the absorption bands²² agree well with those determined experimentally, and the LF-parameters values are not non-realistic.

The assignment (2) results in the orbital order $e_{2g} < a_{1g} \ll e_{1g}$. Some of the calculation results carried out according to this assignment are given in Table II. Comparison of the columns I and II of this Table indicates, that the values of LF-parameters obtained from incomplete matrices do not much differ from those obtained from complete LF-matrices. Also the positions of absorption bands calculated with the use of the both kinds of parameters agree well with experimental positions. This fact justifies the usual application of the simplified LF-theory in the case of d^6 -metallocenes.

The spin-forbidden transitions in $d-d$ spectrum of ferrocene represent a questionable problem not yet definitively solved. Scott and Becker¹³ and McGlynn and co-workers¹⁴ postulated the existence of three very weak bands on the basis of the Gauss analysis of the long-wave part of the band at 22800 cm^{-1} , and they assigned these bands to the three theoretically possible one-electron spin-forbidden $d-d$ transitions ${}^3E_{1g} \leftarrow {}^1A_{1g}$ (14200 cm^{-1}), ${}^3E_{3g} \leftarrow {}^1A_{1g}$ (16100 cm^{-1}), and ${}^3E_{1g} \leftarrow {}^1A_{1g}$ (18500 cm^{-1}). On the basis of detailed spectral studies of several d^6 -metallocenes,

recently Sohn, Hendrickson and Gray¹¹ came to a conclusion that only one spin-forbidden band can be found on the long-wave part of the first spin-allowed band, and they assigned it to the transition ${}^3A_{1g} \leftarrow {}^1A_{1g}$ (18900 cm^{-1} for ferrocene). This problem cannot be solved by LF-theory, because taking the agreement between the calculated and the experimental transition energies as a criterion of correctness of the assignment, we can see (Table II) that the both assignments of the spin-forbidden transitions (column I and III) are acceptable, although it seems that the transition energy from the low-spin ferrocene configuration $e_{2g}^4 a_{1g}^2$ to the high-spin configuration $e_{2g}^3 a_{1g}^1 e_{1g}^2$, ${}^5E_{2g} \leftarrow {}^1A_{1g}$, is too low in the case of the three spin-forbidden bands (column III) (the transition energy from the low-spin to the high-spin configuration of a chemically comparable d^6 -complex with a strong field, $[\text{Fe}(\text{CN})_6]^{4-}$, is about 50000 cm^{-1}). However, recently Herkstroeter found³⁸, with the use of flash kinetic spectrophotometry, a triplet band of ferrocene in the region 14000 cm^{-1} which was also found by Farmilo and Wilkinson³⁹ by the laser photolysis technique, whereby the problem was again revived.

TABLE II
 $d-d$ Spectrum and Ligand-Field Parameters of Ferrocene (in cm^{-1})

$d-d$ Bands	I		II		III	
	ν_{exp}^a	ν_{calc}^c	ν_{exp}^a	ν_{calc}^d	ν_{exp}^b	ν_{calc}^e
${}^1_a E_{1g} \leftarrow {}^1A_{1g}$	21 800	21 770	21 800	22 315	21 800	21 825
${}^1 E_{3g}$	24 000	23 895	24 000	24 775	24 000	24 055
${}^1_b E_{1g}$	30 800	30 620	30 800	30 920	30 800	30 765
${}^1 E_{2g}$		44 240		45 415		44 285
${}^1_a A_{1g}$		44 320		45 910		46 160
${}^3_a E_{1g}$	18 900	18 990	18 900	19 115	14 200	14 295
${}^3 E_{3g}$		21 105		21 440	16 100	16 115
${}^3_b E_{1g}$		22 960		22 960	18 590	18 260
${}^3 A_{2g}$		40 840		41 485		36 075
${}^5 A_{1g}$		40 620		40 715		25 790
${}^5 E_{2g}$		33 690		33 615		18 900

^a ν_{exp} according to ref.¹¹; ^b ν_{exp} of the spin-allowed bands according to ref.¹¹ and ν_{exp} of the spin-forbidden bands according to ref.¹³; ^c the calculated values of LF-parameters: $B = 415$, $C = 1300$, $D_s = 5020$, $D_t = 2630$, $C/B = 3.15$, $D_s/D_t = 1.90$, $D_t/B = 6.35$; ^d LF-parameters were taken from ref.¹¹ and used for calculation of ν_{calc} ; ^e the calculated values of LF-parameters: $B = 440$, $C = 3700$, $D_s = 5260$, $D_t = 2830$, $C/B = 8.41$, $D_s/D_t = 1.86$, $D_t/B = 6.43$.

It is worth-while to mention the comparison of the LF-parameters obtained at low temperature (with three separate spin-allowed bands) with those obtained at normal temperature (two bands). The calculation results for ferrocene showed²² that the obtained value of the parameter *B* is practically independent of the temperature of the spectral measurement. With respect to great similarity of *d-d* spectra of the *d*⁶-metalloenes known so far (Table I) the general validity of the above finding can be presumed. The presumption can be used for examination of the nephelauxetic effect in the series of some *d*⁶-metalloenes, where it is sufficient to carry out the spectral measurements under more convenient experimental conditions (at normal temperature). On the contrary, there is a small difference in spectrochemical quantities (parameters *D_s* and *D_t* and their ratio, overall splitting): the higher-temperature *i.e.* "two-bands" *d-d* spectrum gives a somewhat lower values of overall splitting. Therefore, it is advisable to use spectral data obtained at the same temperature when the spectrochemical properties of various *d*⁶-metalloenes are correlated.

The electron spectra of the *d*⁶-metalloenes given in Table I, which were measured at 298 K, contain (besides the two abovementioned long-wave *d-d* bands of low intensities, the band *I* having the lower energy, and the band *II* corresponding to higher energy) one to three short-wave bands with medium to high intensities, which correspond to CT- or interligand transitions. In the present communication we shall deal with the *d-d* bands only. The spectrum of Ni cb₂ will be discussed as a special case. The spectra of isometallic *d*⁶-metalloenes are similar both in the long-wave and short-wave regions, especially so with Fe cp₂ and [Fe cb₂]²⁻. The higher intensity of the *d-d* bands of carborane complexes as compared with cyclopentadienyl complexes is probably due (besides other possible effects) to the more marked nephelauxetic effect of the cb-ligand and to the lower symmetry of cb-metalloenes (their *D_{∞h}* symmetry is only approximate). The dependence between hyperchromic effect of the *d-d* transitions forbidden by the Laport rule and the nephelauxetic effect was explained by Jørgensen^{40,41}.

The values of LF-parameters and the quantities derived therefrom were calculated for the investigated *d*⁶-metalloenes with the use of experimental energies of the bands *I* and *II* which were, on the basis of analysis of the *d-d* spectrum of ferrocene, assigned to one-electron spin-allowed transitions, *viz* the band *I* to the transitions $\varepsilon_1 = {}^1_aE_{1g} \leftarrow {}^1A_{1g}(e_{1g} \leftarrow a_{1g})$ and $\varepsilon_2 = {}^1E_{3g} \leftarrow {}^1A_{1g}(e_{1g} \leftarrow e_{2g})$, band *II* to the transition $\varepsilon_3 = {}^1_bE_{1g} \leftarrow {}^1A_{1g}(e_{1g} \leftarrow e_{2g})$. With respect to the information obtained from the analysis of *d-d* spectrum of a representative *d*⁶-metalloene using complete LF-matrices, the calculation for the series of compounds was carried out in approximation with limited configuration interaction between the mono-excited LF-states ${}^1E_{1g}$ with the values *C/B* = 4, and *C/B* = 9. The explicite expressions for calculation of the parameters *B*, *D_s*, *D_t* from the energies ε_1 , ε_2 and ε_3 are given in refs^{15,16}. In this approximation the parameter *B* does not depend on the parameter *C*, and

the splitting parameter values D_s and D_t change very little with increasing ratio C/B , their ratio remaining practically constant (see Table III).

In the case of the mixed cyclopentadienyl-carborane complexes of Fe(II) and Co(III) the energies of three $d-d$ transitions were calculated independently with the use of the rule of "average environment" using the parameters (β , D_s , D_t) of the corresponding biscyclopentadienyl and biscarborane complexes: LF-parameter ($M\text{ cp cb}$) = $\frac{1}{2}$ (LF-parameter ($M\text{ cp}_2$) + LF-parameter ($M\text{ cb}_2$)). As it follows from Table IV, the calculated energies agree with the experimental values very well.

Absorption spectrum of biscarborane complex of Ni(IV) differs from those of the other d^6 -metallocenes at first sight (see Table I). Besides the short-wave highly intensive band, which undoubtedly belongs to the CT- or intraligand transition, the spectrum contains only one long-wave considerably intensive band which apparently is not analogous to the I band of the other compounds. In order to get

TABLE III
Ligand-Field Parameters of d^6 -Metallocenes

Parameters	Fe cp_2	Ru cp_2	Co cp_2^+	Fe cb_2^{2-}	Co cb_2^-	Fe cp cb^-	Co cp cb
D_s, cm^{-1}	4 555 ^a	5 289	4 945	3 878	4 200	4 141	4 626
	4 837 ^b	5 476	5 252	4 103	4 414	4 387	4 899
D_t, cm^{-1}	2 854 ^a	3 716	3 099	2 472	2 760	2 623	2 946
	3 080 ^b	3 863	3 343	2 652	2 931	2 820	3 161
B, cm^{-1}	395	258	429	315	300	345	378
$B_{\text{ion}}, \text{cm}^{-1}$ ^c	982	705	1 160 ^d	982	1 160 ^d	982	1 160 ^d
D_s/D_t	1.60 ^a	1.42	1.60	1.57	1.52	1.58	1.57
	1.57 ^b	1.42	1.57	1.55	1.51	1.56	1.55
D_t/B	7.23 ^a	14.43	7.22	7.85	9.20	7.60	7.80
	7.80 ^b	14.97	7.79	8.42	9.77	8.17	8.36
A_{10}, cm^{-1}	23 985 ^a	31 871	26 045	20 842	23 400	22 089	24 834
	25 963 ^b	33 154	28 178	22 417	24 896	22 813	26 711
A_{02}, cm^{-1} ^e	3 950 ^a	2 576	4 285	3 152	3 000	3 449	3 774
	3 948 ^b	2 589	4 293	3 152	3 001	3 448	3 791
A_{12}, cm^{-1}	27 935 ^a	34 447	30 330	23 994	26 400	25 538	28 608
	29 911 ^b	35 743	32 471	25 569	27 897	27 261	30 502

^a Calculated for the ratio $C/B = 4$; ^b calculated for the ratio $C/B = 9$; ^c the values according to ref.⁴²; ^d extrapolated with the use of the values⁴² for Co(O), Co(I), Co(II) and Mn(I), Fe(II); ^e according to the theory it does not depend on C .

at least approximate idea about its nature, we tried to estimate the energies of the $d-d$ transitions for Ni cb_2 . For this purpose we used the values β , D_s , D_t extrapolated from their trend in the series $[Fe\ cb_2]^{2-} - [Co\ cb_2]^-$ (for B_{ion} Ni(IV) the value $1340\ cm^{-1}$ was used which was extrapolated from the B values⁴² in the isoelectronic series Mn(I) - Fe(II) - Co(III) and in the isometallic series Ni(O) - Ni(I) - Ni(II) - Ni(III): $\beta = 0.2$, $D_s = 4500\ cm^{-1}$, $D_t = 3000\ cm^{-1}$. The estimated energies ϵ_1 , ϵ_2 are higher than those of the experimentally found long-wave band (Table IV). Its intensity and position indicate that it has a character different from $d-d$. Probably it is a CT-band which covers (and practically prevents the identification of) the low-intensity $d-d$ bands.

With the use of the found values D_s and D_t the order of the split d -sublevels and their energetical differences $\Delta_{10} = E(e_{1g}) - E(a_{1g})$, $\Delta_{02} = E(a_{1g}) - E(e_{2g})$, as well as the overall splitting $\Delta_{12} = \Delta_{10} + \Delta_{02} = E(e_{1g}) - E(e_{2g})$ were determined. From these values given in Table III it follows that with all the mentioned d^6 -metallocenes the relative order of the d -orbitals is $e_{2g} < a_{1g} < e_{1g}$ and that Δ_{10} is considerably greater than Δ_{02} , which is one of the reasons of the low-spin configuration of these d^6 -systems. This d -orbital scheme stands in accord with not only the results of analysis of $d-d$ spectra of d^3 - and d^8 -metallocenes^{1-6,16} but also with the scheme of the highest occupied and the lowest unoccupied molecular orbitals, which followed from the semi-empirical calculations MO for ferrocene^{16,43,44} and other metallocenes^{16,43-45}. It is worth-while mentioning that the photoelectronic spectrum of ferrocene⁴⁶⁻⁴⁸ shows a reverse order of the d -orbitals e_{2g} and a_{1g} as compared with that of $d-d$ spectrum. This apparent difference was explained by Hendrickson³⁶.

The central atoms of d^6 -metallocenes as well as some d^3 - and d^8 -metallocenes can be arranged according to the Δ_{12} values in a spectroscopical series: Ni(II) < V(II) < Cr(III) < Fe(II) < Co(III) < Ru(II) < Ni(IV). By a similar comparison it can be seen that spectrochemical order of the both sandwich ligands is $cb < cp$. Carborane anion $(1,2-B_9C_2H_{11})^{2-}$, being a particle with two negative charges, shows a smaller

TABLE IV

Calculation of Energy of the Spin-Allowed One-Electronic $d-d$ Transitions of Carborane Complexes of Fe(II), Co(III) and Ni(IV)

	[Fe cp cb] ⁻		Co cp cb		Ni cb ₂	
	calculated	experimental	calculated	experimental	calculated	experimental
ϵ_1, cm^{-1}	21 357	21 050	23 636	23 700	25 220	23 600
ϵ_2, cm^{-1}	21 364	21 050	23 637	23 700	25 320	23 600
ϵ_3, cm^{-1}	28 439	27 950	30 916	31 250	30 620	33 600

strength of the ligand field than the ligand $C_5H_5^-$ which bears one negative charge. Therefrom we can judge that the proper "sandwich-active" part of the carborane ligand (the open quasi-pentagonal face $B_3C_2H_5$) carries maximum one negative charge. The other negative charge is obviously localized in the "non-sandwich" part, *i.e.* in the bottom part of the carborane "pot". The same finding was obtained from analysis of NQR-spectra⁴⁹ of $[Co\ cp_2]^+$ and $[Co\ cb_2]^-$ and of $d-d$ spectra of metallocenes of $Cr(III)^1$.

The individual d^6 -central atoms with further d^3 - and d^8 -metallocenes atoms can be arranged according to the nephelauxetic parameter β in a nephelauxetic series: $Ni(IV) (?) < Ru(II) \leq Co(III) < Fe(II) < Ni(II) < Cr(III) < V(II)$. The nephelauxetic order of the used sandwich ligands is $cb < cp$ (the carborane ligand is more effective than cyclopentadienyl). The parameter β is connected with the central-field covalency and the symmetry-restricted covalency, both of which form the basis of the nephelauxetic effect, by the relation⁴⁰

$$\beta = a^4(Z_{\text{eff}} + z^*) / (Z + z^*), \quad (5)$$

where a is the mixing coefficient of d -orbital in the normalized molecular orbital $|MO\rangle = a|nd\rangle + b|lig\rangle$ (in the approximation used the coefficients a are the same for all the d -functions), Z_{eff} is the effective charge of the central ion in the complex, Z is the ionic charge, and z^* is a constant. In the given case, where the separation of the both contributions is impossible, the nephelauxetic effect was interpreted

TABLE V

Interpretation of Nephelauxetic Effect in d^6 -Metallocenes^a

d^6 -metallocene	β	A	B	C	
		pure central-field covalency	pure symmetry-restricted covalency	equal contribution of the both covalencies	
		Z_{eff}	a^2	Z_{eff}	a^2
Fe cp_2	0.40	-0.69	0.63	0.35	0.80
Ru cp_2	0.37	-0.86	0.60	0.22	0.78
Co cp_2^+	0.37	-0.47	0.61	0.84	0.78
Fe $cb_2^2^-$	0.32	-1.06	0.57	0.05	0.75
Fe $cp\ cb^-$	0.35	-0.92	0.59	0.17	0.77
Co cb_2^-	0.26	-1.08	0.51	0.30	0.71
Co $cp\ cb$	0.33	-0.71	0.57	0.64	0.76

^a For all the nd^6 -ions the value $z^* = 2.5$ was used (according to ref.⁴⁰).

(Table V) as a result of A) pure central-field covalency ($a^2 = 1$), B) pure symmetry-restricted covalency ($Z_{\text{eff}} = Z$), C) equal contributions of the both. We suppose that the real situation in biscyclopentadienyl d^6 -metallocenes is close to the interpretation C for the following reasons: 1) the value $a^2 \approx 0.80$ is close to those of MO-calculations^{16,17,43} (a^2 : for $a_{1g} = 1$, for $e_{1g} = 0.92$, for $e_{2g} = 0.83$); 2) the Z_{eff} values are close to those found from the X-ray absorption spectra (Fe cp_2 : +0.4, Co cp_2^+ : +0.6) (ref.⁵⁰); 3) the lower Z_{eff} value of Ru cp_2 as compared with Fe cp_2 agrees with some experimental facts, e.g. the lower reactivity of Ru cp_2 in electrophilic substitution reactions³⁴ or the lower frequencies of the valence C—C vibrations of the rings in Ru cp_2 as compared with those of ferrocene⁵¹. Evaluation of the situation with the carborane d^6 -metallocenes is still more difficult due to the lack of reference data. If again the interpretation C were considered the most acceptable, then it would be found that the substitution of cyclopentadienyl by the carborane ligand in an isometallic d^6 -complex results in a marked decrease of Z_{eff} . This fact agrees with the known tendency of the cb-ligand to stabilize the complexes with central ions in a higher oxidation state and destabilize the complexes with central ions in a lower oxidation state.

REFERENCES

1. Pavlík I., Černý V., Maxová E.: This Journal 37, 171 (1972).
2. Pavlík I., Maxová E., Černý V.: Proc. 2nd Conf. Coord. Chem., p. 189, Bratislava—Smolenice 1969.
3. Pavlík I., Černý V., Maxová E.: This Journal 35, 3045 (1970).
4. Pavlík I., Maxová E., Večerníková E.: Z. Chem. 12, 26 (1972).
5. Pavlík I., Maxová E.: Proc. 3rd Conf. Coord. Chem., p. 247, Bratislava—Smolenice 1971.
6. Pavlík I., Maxová E., Klikorka J.: Sb. Věd. Pr., Vys. Šk. Chemickotechnol., Pardubice 32, 11 (1974).
7. Wilkinson G., Cotton F. A.: Progr. Inorg. Chem. 1, 1 (1959).
8. Hawthorne M. F.: J. Amer. Chem. Soc. 90, 879 (1968).
9. Stephenson P. B., Winterrowd W. E.: J. Chem. Phys. 52, 3308 (1970).
10. Sohn Y. S., Hendrickson D. N., Smith J. H., Gray H. B.: Chem. Phys. Lett. 6, 499 (1970).
11. Sohn Y. S., Hendrickson D. N., Gray H. B.: J. Amer. Chem. Soc. 93, 3603 (1971).
12. Scott D. R., Becker R. S.: J. Chem. Phys. 35, 516 (1961).
13. Scott D. R., Becker R. S.: J. Organometal. Chem. 4, 409 (1965).
14. Armstrong A. T., Smith F., Elder E., McGlynn S. P.: J. Chem. Phys. 46, 4321 (1967).
15. Scott D. R.: J. Organometal. Chem. 6, 429 (1966).
16. Prins R.: Thesis. Univ. Amsterdam 1967.
17. Krieger R., Voithländer J.: Z. Naturforsch. 27a, 1444 (1972).
18. Robertson R. E., McConnell H. M.: J. Phys. Chem. 64, 70 (1960).
19. Scott D. R., Matsen F. A.: J. Phys. Chem. 72, 16 (1968).
20. Piper T. S., Carlin R. L.: J. Chem. Phys. 33, 1208 (1960).
21. Černý V.: This Journal 38, 317 (1973).
22. Archives of the Department of General and Inorganic Chemistry. p. Vys. Šk. Chemickotechnol., Pardubice.

23. Ferguson J., Wood D. L.: *Aust. J. Chem.* **23**, 861 (1970).
24. Witzke H.: *Theor. Chim. Acta* **20**, 171 (1971).
25. König E., Thomas G.: *J. Inorg. Nucl. Chem.* **34**, 1173 (1972).
26. Wilkinson G.: *Org. Syn.* **36**, 31 (1955).
27. Wilkinson G.: *J. Amer. Chem. Soc.* **74**, 6146 (1965).
28. Rauch M. D., Fischer E. O., Grubert H.: *J. Amer. Chem. Soc.* **82**, 76 (1960).
29. Wilkinson G.: *J. Amer. Chem. Soc.* **74**, 6148 (1952).
30. Warren L. F., Hawthorne M. F.: *J. Amer. Chem. Soc.* **89**, 470 (1967).
31. Pavlík I., Foniok R., Grégr J.: *Sb. Věd. Pr., Vys. Šk. Chemickotechnol., Pardubice*, p. 25, 1967/I.
32. Rosenblum M.: *Chemistry of the Iron Group Metallocenes, Part I*. Interscience, New York 1965.
33. Coutière M. M., Demuyneck J., Veillard A.: *Theor. Chim. Acta* **27**, 281 (1972).
34. Rohmer M. M., Veillard A., Wood M. H.: *Chem. Phys. Lett.* **29**, 466 (1974).
35. Ballhausen C. J., Gray H. B. in the book: *Coordination Chemistry*, Vol. 1. p. 3. ACS Monograph No 168, Washington 1971.
36. Hendrickson D. N.: *Inorg. Chem.* **11**, 1161 (1971).
37. Nielson D., Boone D., Eyring H.: *J. Phys. Chem.* **76**, 511 (1972).
38. Herkstroeter W. G.: *J. Amer. Chem. Soc.* **97**, 4161 (1975).
39. Farmilo A., Wilkinson F.: *Chem. Phys. Lett.* **34**, 575 (1975).
40. Jørgensen C. K.: *Progr. Inorg. Chem.* **4**, 73 (1962).
41. Jørgensen C. K.: *Modern Aspects of Ligand Field Theory*. North-Holland, Amsterdam—London 1971.
42. Tondello E., De Michelis G., Oleari L., Di Sipio L.: *Coord. Chem. Rev.* **2**, 65 (1967).
43. Schachtschneider J. H., Prins R., Ros P.: *Inorg. Chim. Acta* **1**, 462 (1967).
44. Armstrong A. T., Carroll D. G., McGlynn S. P.: *J. Chem. Phys.* **47**, 1104 (1967).
45. Rettig M. F., Drago R. S.: *J. Amer. Chem. Soc.* **91**, 3432 (1969).
46. Turner D. W. in the book: *Physical Methods in Advanced Inorganic Chemistry* (H. Hill, P. Day, Eds), Chapter 3. Interscience, New York 1968.
47. Turner D. W.: *Advan. Mass Spectrom.* **4**, 755 (1968).
48. Rabelais J. W.: *J. Chem. Phys.* **57**, 1185 (1972).
49. Harris C. B.: *Inorg. Chem.* **7**, 1517 (1968).
50. Barinskii R. L.: *Zh. Strukt. Khim.* **1**, 200 (1960).
51. Fritz H. P.: *Advan. Organometal. Chem.* **1**, 240 (1964).

Translated by J. Panchartek.