Electronic spectra and electron structure of fullerene complex $(\eta^2\text{-}C_{60})Fe(CO)_4$

S. I. Gorel'sky,[a*] **T. V. Magdesieva,**[b] **and K. P. Butin**[b]

[a]*Higher School of Materials Sciences, M. V. Lomonosov Moscow State University,*
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 0998
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 5546

The electronic spectrum of the $C_{60}Fe(CO)_4$ complex was studied in a toluene solution. The more intense absorption of $C_{60}Fe(CO)_4$ in the visible region, relative to the free C_{60}, can be attributed to the effect of lower symmetry of the C_{60} fullerene cage in $C_{60}Fe(CO)_4$ and, thus, relaxation of selection rules for forbidden internal electronic transitions of C_{60}. No bands of the charge transfer from 3d(Fe) to C_{60} orbitals were observed in the visible region of the complex spectrum. Assignment of the bands was confirmed by semiempirical calculations of the electronic spectrum.

Key words: fullerenes; icosahedral complexes; electronic spectra; iron carbonyl; semiempirical calculations.

Easy access to macroscopic quantities of fullerene C_{60} allows one to obtain and investigate its versatile derivatives and, in particular, its complexes with transition metals.

Electronic spectra of the η^2-complexes of fullerene C_{60} with elements of the second and third transition series in the visible region are very similar and weakly depend on the nature of the metal coordinated by fullerene (Table 1). The overwhelming majority of monometallic complexes of C_{60} are intense green in solution due to a charge transfer from the metal atom to the C_{60} ligand (CTML) and to intraligand transitions in C_{60}, which are more intense in complexes than in the free fullerene.[1]

Electronic spectra of metal complexes of the first transition series metals have not been studied until recently. The aim of this work is to investigate the electronic spectrum of the $C_{60}Fe(CO)_4$ complex, the synthesis of which was described previously.[5]

Results and Discussion

The electronic spectrum of a solution of $C_{60}Fe(CO)_4$ (**1**) in toluene in the visible and near-UV region is shown in Fig. 1. In contrast to the free C_{60}, complex **1** is characterized by the more intensive absorption in that spectral region where the C_{60} bands (from 15000 cm^{-1})

Table 1. Electron spectroscopy data (visible and near-UV region) for η^2-complexes of C_{60} in solution

Complex	Solvent	Transition energy, E/1000 cm^{-1} (log ε)		Reference
		$d(M)-t_{1u}(C_{60})$[a]	$d(M)-t_{1g}(C_{60})$[b]	
$C_{60}[Pd(PPh_3)_2]_n$,				
n = 1	Toluene	15.1 sh, 16.3 (3.7)	22.7 (4.0)	1
n = 2		16.5 (4.1)	23.0 (4.4)	
n = 4		20.0 (4.5)	26.0 (4.8)	
$C_{60}Rh(acac)(Py)$	C_6H_6+Py (20 %) mixture	16.1 sh, 17.1 (3.6)	23.3 (4.1)	2
$C_{60}IrH(CO)(PPh_3)_2$	THF	15.6 sh, 16.5 (3.6)	23.0 (4.0)	3
$C_{60}Ir(CO)(C_9H_7)$	CH_2Cl_2	15.6 sh, 16.9 (3.6)	22.9 (3.9)	4

[a] CTML $d(M)-t_{1u}(C_{60})$ and $h_u-t_{1u}(C_{60})$ transitions are overlapped. [b] CTML $d(M)-t_{1g}(C_{60})$ and $h_u-t_{1g}(C_{60})$ transitions are overlapped.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1453—1458, June, 1996.

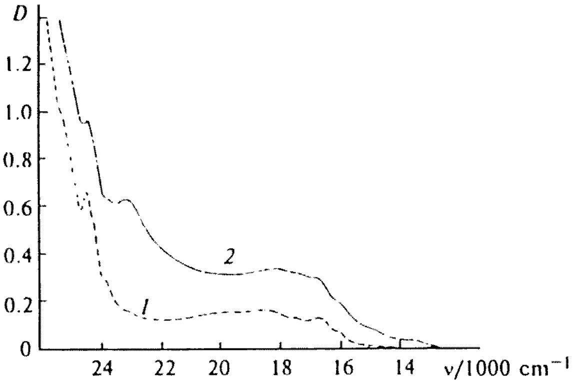

Fig. 1. Electronic spectra of C_{60} (**1**) and $C_{60}Fe(CO)_4$ (**2**) complexes (dotted and solid line, respectively) in visible region. Solutions of $2.2 \cdot 10^{-4}$ mole L^{-1} in toluene, optical path 1 cm.

lie and also by additional peaks at 13500 ($\log\varepsilon = 2.2$), 14800 ($\log\varepsilon = 2.5$), and 23200 cm^{-1} ($\log\varepsilon = 3.5$). Complex $Fe(CO)_5$ with the absorption bands at 35500 cm^{-1} ($\log\varepsilon = 3.6$), 41500 cm^{-1} ($\log\varepsilon = 4.0$), and 41700 cm^{-1} ($\log\varepsilon = 4.2$) assigned to the d—d-transition (5e′—5a$_1$′) and 3d(Fe)→π*(CO) CTML-transitions 5e′—6e′ and 5e′—2a$_2$′, respectively,[6] does not absorb in the visible region. Therefore, bands assigned to the 3d(Fe)→π*(CO) CTML-transitions of $C_{60}Fe(CO)_4$ should not occur in the visible region.

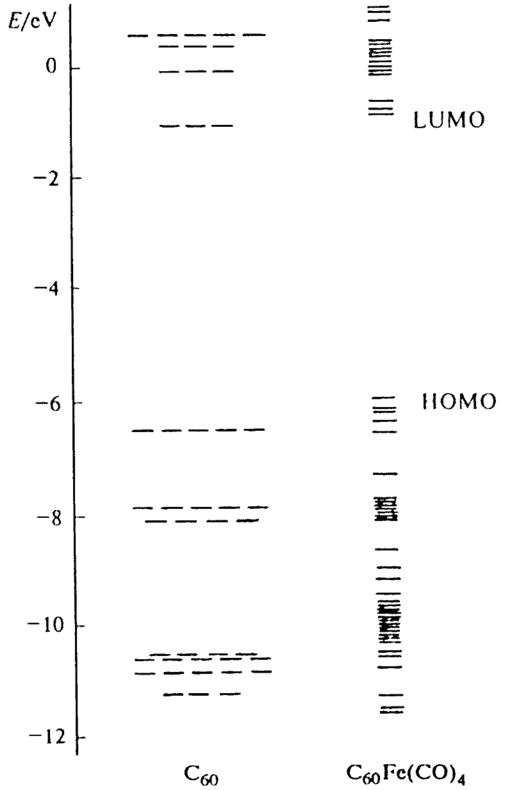

Fig. 2. Energies of molecular orbitals of C_{60} and $C_{60}Fe(CO)_4$ complexes calculated by the ZINDO/S method (interval from −12 eV to 1 eV).

In the case of free C_{60} (the symmetry point group I_h, the ground state ^1A_g with completely filled levels) the electronic transitions to the $^1T_{2g}$, $^1T_{1g}$, ^1G_g, and ^1H_g states corresponding to the electron transfer from the highest occupied molecular orbital (HOMO) h_u to the lowest unoccupied molecular orbital (LUMO) t_{1u} are forbidden.[7—9] The electron transfer from HOMO h_u to the t_{1g} orbital (LUMO+1) gives the following electronic states: $^1T_{2u}$, ^1H_u, ^1G_u, and $^1T_{1u}$. The transition between the ^1A_g and $^1T_{1u}$ states is favored; it occurs at 24500 cm^{-1} ($\log\varepsilon = 3.5$). The forbidden transitions to the $^1T_{2g}$, $^1T_{1g}$, ^1G_g, ^1H_g, $^1T_{2u}$, ^1H_u and ^1G_u states are observed as weak bands in the 15000—24000 cm^{-1} region (see Refs. 7—9).

Formation of **1** (C_{2v} point symmetry) results in the distortion of icosahedral structure of the carbon cage,[1] which causes the splitting of degenerate electronic levels of C_{60} and a partial removal of exclusion from the forbidden electronic transitions. The splitting mentioned above is small and amounts to 1000—3000 cm^{-1} for monometallic complexes (see Ref. 10). Thus, the en-

Table 2. Energies of spin-favorable electronic transitions (E) of $C_{60}Fe(CO)_4$ complex (to 26000 cm^{-1}) calculated by ZINDO/S method with the configuration interaction of 17×22 size[8—9] (749 singly excited configurations)

E /1000 cm^{-1}	f[a]	Orbital[b]	Orbital symmetry[b]	Term of excited state
15.82	0	144—146	b_2—b_1	$^1A_2$
16.40	0.0054	144—145	b_2—a_1	$^1B_2$
17.39	0.0001	142—145	b_1—a_1	$^1B_1$
17.46	0.0001	143—146	a_2—b_1	$^1B_2$
17.74	0	143—145	a_2—a_1	$^1A_2$
18.55	0.0015	144—147,142—146	b_2—b_2,b_1—b_1	$^1A_1$
19.42	0	142—147,141—145	b_1—b_2,a_2—a_1	$^1A_2$
20.34	0.0001	141—146	a_2—b_1	$^1B_2$
20.35	0.0006	140—146	a_2—b_2	$^1B_1$
20.50	0.0029	143—147,141—147	a_1—b_1,a_2—b_2	$^1B_1$
20.78	0.0107	144—147,142—146	b_2—b_2,b_1—b_1	$^1A_1$
21.28	0	142—147,141—145	b_1—b_2,a_2—a_1	$^1A_2$
22.25	0.0002	143—147,140—146	a_2—b_2,a_1—b_1	$^1B_1$
22.85	0.0209	140—147	a_1—b_2	$^1B_2$
23.09	0.0003	140—145	a_1—a_1	$^1A_1$
23.69	0	144—154	b_2—b_1	$^1A_2$
23.86	0.0018	142—153	b_1—a_2	$^1B_2$
24.06	0.0089	143—153	a_2—a_2	$^1A_1$
24.53	0.0068	144—148	b_2—a_2	$^1B_1$
25.08	0	143—154,142—153	a_2—b_1,b_1—a_2	$^1B_2$
25.45	0.0017	142—154	b_1—b_1	$^1A_1$
25.74	0.0148	144—153	b_2—a_2	$^1B_1$

[a] The oscillator strength. [b] The number and symmetry of the orbitals that make the largest contribution to the corresponding electronic transition (the coefficient at the Slater determinant is larger than 0.3); HOMO is the 144th orbital, LUMO is the 145th one.

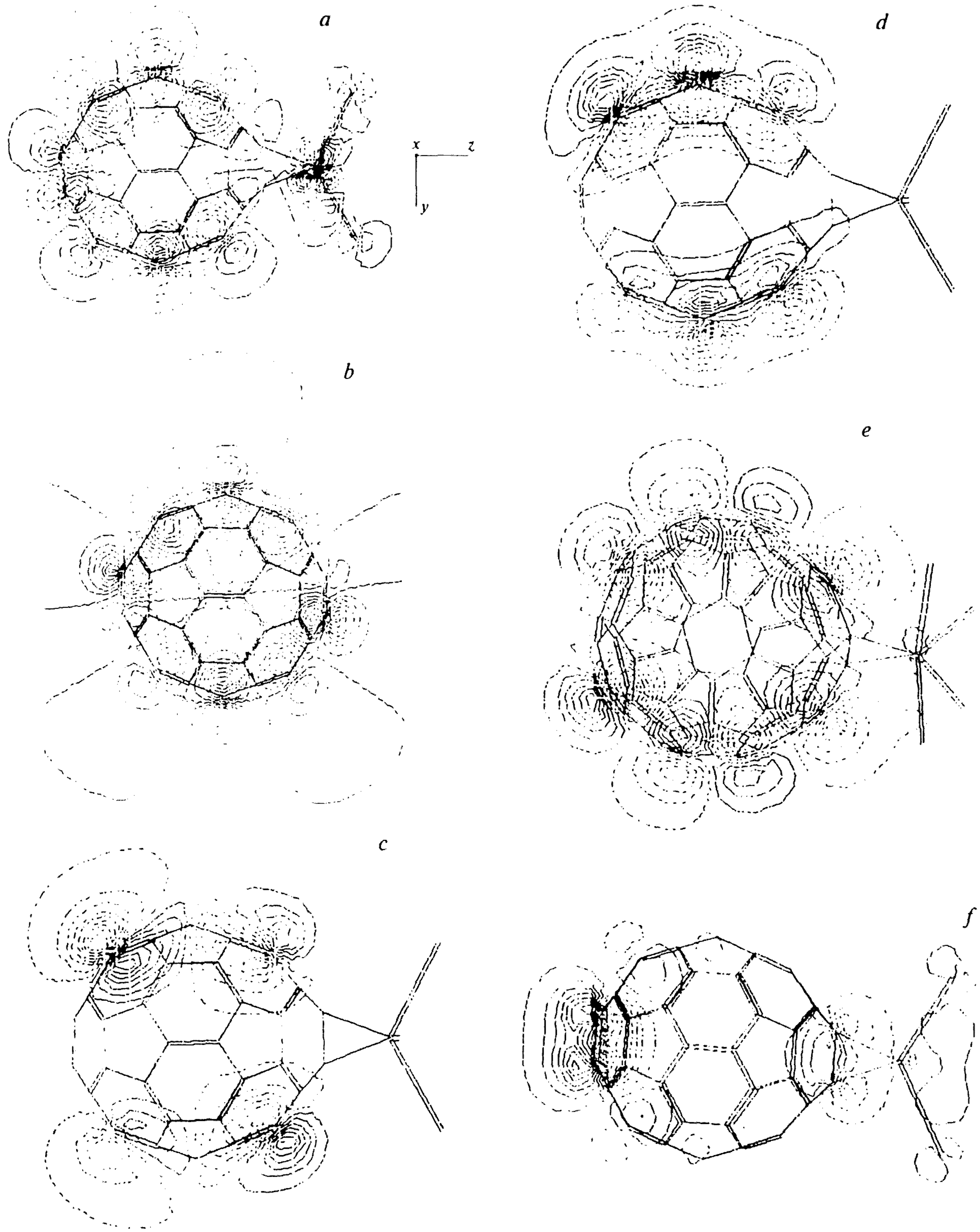

Fig. 3. Contour diagrams of HOMOs of $C_{60}Fe(CO)_4$ (*a—e*) and C_{60} (*f*) complexes: *a*, symmetry b_2, $E = -6.05$ eV; *b*, symmetry a_2, $E = -6.25$ eV; *c*, symmetry b_1, $E = -6.26$ eV; *d*, symmetry a_2, $E = -6.44$ eV; *e*, symmetry a_1, $E = -6.66$ eV; *f*, symmetry h_u, $E = -6.59$ eV; dotted and solid lines are the isolines of the opposite sign.

ergy levels of C_{60} in complex **1** change slightly, and its more intense absorption in the visible region can be explained by partial removal of exclusion from the forbidden electronic transitions of C_{60}.

One could assume that the relatively intense band at 23200 cm^{-1} is due to the 3d(Fe)—t_{1u}*(C_{60}) CTML. However, the same band is observed in the electronic spectra of such low-symmetry fullerene derivatives as $C_{60}CH_2$ [11] and $C_{60}O$ [12] (C_{2v} symmetry point group) and is assigned to the C_{60} cage. Additionally, unlike the donor metal groups (for instance, $Pd(PPh_3)_2$), the $Fe(CO)_4$ group has an electron affinity close to that of C_{60} (−2.4 eV[13] and −2.7 eV for free C_{60},[14] respectively) and is not a donor group with respect to fullerene. Therefore one can conclude that low-energy bands of 3d(Fe)—t_{1u}*(C_{60}) CTML should not be observed in the spectrum of complex **1**. Those transitions as well as the 3d(Fe)—π*(CO) CTML should lie in the UV-region of the spectrum overlapping the intensive absorption of C_{60}.

To test the assignment of the bands we carried out semiempirical quantum-chemical calculations of the electron structure and spectra of C_{60}, $C_{60}Fe(CO)_4$, and $C_2F_4Fe(CO)_4$ molecules using the ZINDO/S method.[15–17] The most important characteristics obtained are represented in Fig. 2 and in Table 2. The results of the calculations of the electron structure of C_{60} nearly coincide with those previously obtained by the CNDO/S[8] and INDO/S[9] methods. For instance, the energy of the HOMO h_u is −6.59 eV (ZINDO/S), −6.57 eV (INDO/S),[9] and −7.81 eV (photoelectron spectroscopy).[18]

As is seen from Fig. 2, the coordination of $Fe(CO)_4$ with C_{60} results in the splitting of degenerate electronic levels of the latter. In the complex formed d-orbitals of the Fe atom are mixed with the carbon cage orbitals of suitable symmetry. The occupied orbitals with the large contribution of d-orbitals of the Fe atom possess a fairly low energy (lower than −9.08 eV); it is comparable with calculated energies of d-orbitals of the Fe atom in the $C_2F_4Fe(CO)_4$ complex (from −10.1 to −11.2 eV). The five HOMOs in complex **1** (Fig. 3) with symmetry b_2, a_2, b_1, a_1, and a_2 are formed mainly by the splitted HOMO of fullerene ($h_u = a_1 + 2a_2 + b_1 + b_2$) as could be expected from the group theory concept[1] (the chosen standard coordinate system is shown in Fig. 3). It is clearly seen in Fig. 3 that all of these five orbitals are formed by the h_u-orbital of C_{60}, odd with respect to the inversion center.

The next nine occupied orbitals are formed by splitted h_g and g_g orbitals ($3a_1 + 2a_2 + 2b_1 + 2b_2$). Three LUMOs of complex $C_{60}Fe(CO)_4$ (Fig. 4) are mainly formed by the splitted LUMO of fullerene ($t_{1u} = a_1 + b_1 + b_2$), while the next three above-lying orbitals are formed by the splitted LUMO+1 of fullerene ($t_{1g} = a_2 + b_1 + b_2$), the splitting of the t_{1u} being equal to 0.21 eV. In complex $C_{60}Pt(PH_3)_2$ the splitting t_{1u} was estimated as 0.35 eV.[10]

Therefore, the transitions from HOMO to LUMO in the visible region (the lowest-energy bands) are associated with the absorption of the fullerene cage in complex **1**. The absence of the intensive bands of the CTML sets off **1** from other known C_{60} complexes with transition metals.

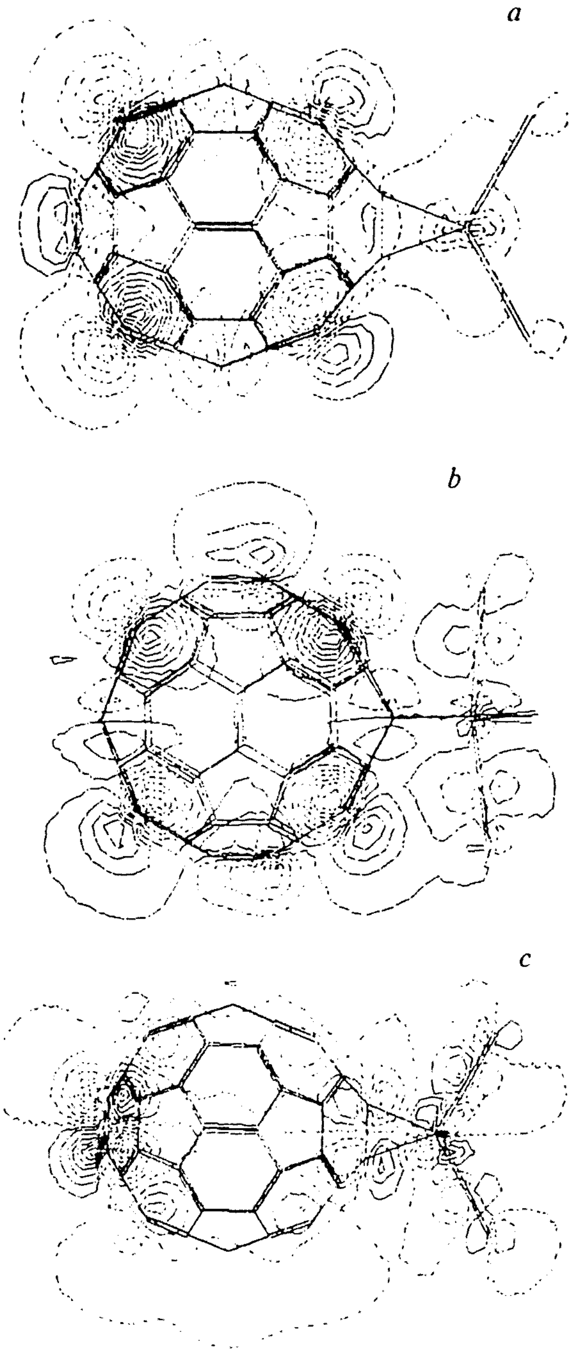

Fig. 4. Contour diagram of the $C_{60}Fe(CO)_4$ complex: *a*, symmetry a_1, E = −0.87 eV; *b*, LUMO+1 symmetry b_1, E = −0.87 eV; *c*, LUMO+2 symmetry b_2, E = −0.66 eV.

The calculated electronic spectrum well reproduces the experimental spectrum. The energies of the spin-favorable electronic transitions of $C_{60}Fe(CO)_4$, their oscillator strengths as well as the numbers and the symmetry of the orbitals that make the largest contributions to the corresponding electronic transitions are listed in Table 2. Since the ground state of molecule **1** is described by the $^1A_1$ term (perfectly filled levels), the transitions to excited states with $^1A_1$, $^1B_1$, and $^1B_2$ terms are permitted, whereas those to the state with $^1A_2$ term are forbidden (see table of the characters of irreducible representations of C_{2v} group, for instance, Ref. 6). For the latter case such integral characteristic of the intensity of absorption as oscillator strength is equal to zero.[19] However, these transitions can be observed in the spectrum as weak bands due to vibronic interactions.[20]

We also calculated the energies of the forbidden singlet-triplet electronic transitions. The first of them ($^1A_1$—$^3A_2$, from 144th to 146th orbital with spin flip), with the energy of 11670 cm^{-1}, is both symmetry and spin-forbidden; it should be of very weak intensity. The second singlet-triplet transition is expected to be at 13400 cm^{-1}. A total of 32 singlet - triplet transitions correspond to the region extending to 26000 cm^{-1}.

It is of interest to compare the calculated values of the oscillator strengths of the electronic transitions with those obtained from the experimental electronic spectrum of complex **1**. The sum of calculated oscillator strengths for transitions in the interval 15000—21500 cm^{-1} is equal to 0.0214 whereas the experimental value equals 0.038. For transitions in the interval 15000—26000 cm^{-1} the sum of calculated oscillator strengths is equal to 0.0768 while the experimental value equals 0.093. Thus, the calculated values agree with the experimental ones.

Experimental

$C_{60}Fe(CO)_4$ was synthesized using the procedure described previously.[5] Toluene of "pure" grade was boiled for 3 h over Na and distilled. Electronic spectra of the solutions of C_{60} and $C_{60}Fe(CO)_4$ in toluene were registered on a Specord UV-Vis spectrophotometer in quartz cells with optical path of 0.5 and 1 cm, respectively.

Quantum-chemical calculations of electronic spectra were carried out using the semiempirical ZINDO/S method incorporated in the HyperChem Release 3 for Windows program. The geometry of the complexes was optimized beforehand by the MM+ method.[21] Several calculated interatomic distances and bond angles are listed in Table 3.

Only valence atomic orbitals were taken into account in calculations of the electron structure of complexes. The weighting coefficients in evaluation of the resonance integrals were equal to 1.267 for σ—σ-overlap and 0.640 for π—π-overlap, as recommended in previous publications.[22—23] Once the difference between the electronic energy in the preceding and the subsequent cycles had become less than 0.3 kcal $mole^{-1}$, the calculations were stopped. Following the calculations of the energies and MO coefficients, the calculations of the matrix of the configuration interaction[8—9] were carried out (only singly excited states were taken into account, in particular, for complex **1** from 17th HOMO to 22nd LUMO, *i.e.*, 749 electronic configurations), as well as of the energies of electronic transitions and their oscillator strengths.

Table 3. Interatomic distances (*d*) and bond angles (ω) calculated by the MM+ method and used in calculations of the electron structure

Complex	Bond	*d*/Å	
		Calculation	Experiment
$C_2F_4Fe(CO)_4$	C—C	1.479	1.530[24]
	Fe—C(C_2F_4)	2.019	1.989[24]
	Fe—$C(CO)_{eq}$	1.784	1.846[24]
	Fe—$C(CO)_{ax}$	1.786	1.823[24]
	C—O	1.162	1.138[24]
$C_{60}Fe(CO)_4$	C—C(6—6)(C_{60}), coord. to Fe	1.454	
	C—C(C_{60})	1.346	
	Fe—C(C_{60})	2.009	
	Fe—$C(CO)_{eq}$	1.785	
	Fe—$C(CO)_{ax}$	1.786	
	C—O	1.162	
C_{60}	C—C(6—6)	1.398*	1.387*[25]
	C—C(5—6)	1.451*	1.450*[25]

Complex	Angles	ω/deg	
		Calculation	Experiment
$C_2F_4Fe(CO)_4$	C(CO)—Fe—$C(CO)_{ax}$	173	178.7[24]
	C(CO)—Fe—$C(CO)_{eq}$	117	104.2[24]
$C_{60}Fe(CO)_4$	C(CO)—Fe—$C(CO)_{ax}$	170.7	
	C(CO)—Fe—$C(CO)_{eq}$	123.0	

* Optimization by ZINDO/1 method (see Ref. 17).

The authors express their gratitude to I. V. Arkhangel'sky (M. V. Lomonosov Moscow State University) for providing the C_{60} fullerene samples, S. P. Gubin (N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow) for providing the $Fe_2(CO)_9$ sample, S. P. Knyazev (M. V. Lomonosov Moscow State Academy of Fine Chemical Technology) for help in performing quantum-chemical calculations.

This work was financially supported by the International Science Foundation (Grant 246_s) and the Russian Foundation for Basic Research (Project No. 94-03-08628a).

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Received December 6, 1995