Physical Chemistry

Fullerene C_{60} as a η^5- and η^6-ligand in sandwich-type π-complexes with transition metals

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The molecular and electronic structures of some hypothetical sandwich-type π-complexes of transition metals with fullerene C_{60} were modeled. The M—C_{60} bonds in η^5-C_{60}MCp$^+$ complexes (M = Fe, Ru, Os) are less strong than the M—Cp bonds in ferrocene, ruthenocene, and osmocene, respectively. The η^6-$C_{60}MC_6H_6$ complexes (M = Cr, Mo, W) should be less stable than their classical analogs $(C_6H_6)M(C_6H_6)$. The coordination of a metal atom with the fullerene at its pentagonal face is more energetically favorable than at a hexagonal face.

Key words: fullerenes, π-complexes, transition metals, quantum-chemical calculation.

The stable fullerene *exo*-complexes identified to date are either the usual structures with σ-bonding at a carbon atom or π-olefinic forms with coordination at a C=C bond of the C_{60} cluster.[1] In principle, apart from these fullerene complexes, complexes of other types can form. Among these, η^5-π-cyclopentadienyl and η^6-π-arene complexes are particularly interesting. However, these complexes have not yet been obtained, and questions arise concerning their stability and specific properties in comparison to those of the typical sandwich-type systems, CpMCp and $(C_6H_6)M(C_6H_6)$, where M is a transition metal atom.*

In the present work we modeled the structure and estimated the relative stability of some hypothetical η^5- and η^6-complexes [C_{60}MCp$^+$ and $C_{60}M(C_6H_6)$] and compared them to classical sandwich-type compounds, CpMCp and $(C_6H_6)M(C_6H_6)$. The calculations of the fullerene π-complexes studied were performed in the valent approximation using the expanded Hückel method (EHM)[3] assuming that the structure of the carbon framework does not change significantly when a complex is formed. The C—C bonds in C_{60}, which are common to five- and six-membered rings (the 5,6-bonds), had the length of 1.456 Å, while the 6,6-bonds were 1.401 Å long.

The results of our calculations for the C_{60} cluster coincide with those reported in the literature.[5] In particular, the occupied and vacant energy levels are separated by a 1.558 eV zone, which is close to the value

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* It should be noted that C_{60} complexes with two metal atoms coordinated at non-neighboring faces may be chiral and, hence, can exist in an optically active form.[2]

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determined experimentally from photoemission spectra (1.7 eV, *cf.* Ref. 5). When we modeled the structures of the sandwich-type complexes we also used the results presented in Ref. 6 where the principal laws of the variation of ligand—metal distances in π-complexes of transition metals have been analyzed.

Qualitative estimation of the ability of fullerene C_{60} to form sandwich-type η^5- and η^6-π-complexes

Fullerene C_{60} has a closed electronic shell, *i.e.*, all of its bonding MOs are occupied by electron pairs. Of the many MOs, there always exist suitable ones having σ-symmetry and MO pairs having π-symmetry relative to the axis passing through the center of a given pentagonal or hexagonal fullerene face, *i.e.*, these MOs are capable of symmetry-permitted interaction both with an unoccupied σ-type orbital and with a pair of unoccupied π-type orbitals of a transition metal atom in a MCp^+ moiety (M = Fe, Ru, Os) or $M(C_6H_6)$ (M = Cr, Mo, W). The degree of this interaction depends on the mutual orientation of the MO fragments, on the coefficients of the AOs constituting these MOs, and on their relative energy.

As an example, let us perform a comparative analysis of the interaction of a MCp^+ cation with a cyclopentadienyl anion, on the one hand, and with a five-membered cycle of corannulene $C_{20}H_{10}$ (CA), on the other hand. The carbon framework of CA is isostructural to the fragments of fullerene C_{60}, which contains a five-membered cycle framed by hexagons. Hence, the CA molecule can serve as a convenient model in analyzing the ability of fullerene C_{60} to form η^5-π-complexes $C_{60}MCp^+$.

In this respect, let us consider the MOs of corrannulene obtained in the topological approximation. We shall separate components corresponding to its five-membered ring and express them *via* MOs of the cyclopentadienyl anion. An analysis of these expressions for 10 bonding MOs of CA indicates that there exist two groups of MOs (Ψ_1, Ψ_2, Ψ_3 and Ψ_4, Ψ_7, Ψ_8) most similar to the corresponding bonding MOs (ϕ_1, ϕ_2, ϕ_3) of the cyclopentadienyl anion. These MOs of CA can be represented as follows:

$$\begin{array}{lll}
\Psi_1(\mathrm{CA}) = 0.75\phi_1 & (a_1) & \varepsilon_1 = 2.67\beta \\
\Psi_2(\mathrm{CA}) = 0.11\phi_2+0.40\phi_3 & (e_1) & \varepsilon_2 = 2.11\beta \\
\Psi_3(\mathrm{CA}) = -0.40\phi_2+0.11\phi_3 & (e_1) & \varepsilon_3 = 2.11\beta \\
\Psi_4(\mathrm{CA}) = 0.61\phi_1 & (a_1) & \varepsilon_4 = 1.51\beta \\
\Psi_7(\mathrm{CA}) = 0.20\phi_2+0.74\phi_3 & (e_1) & \varepsilon_7 = 0.78\beta \\
\Psi_8(\mathrm{CA}) = -0.74\phi_2+0.20\phi_3 & (e_1) & \varepsilon_8 = 0.78\beta
\end{array}$$

Here β is the resonance integral and ε_j is the orbital energy of the Ψ_j MO of the corresponding symmetry (a_1 or e_1).

Thus, because of delocalization of the π-electron density in CA along a more extended system than in the case of a Cp ring, the coefficients at the AOs of atoms in the five-membered ring for bonding MOs of CA are much lower than in the case of an isolated cyclopentadienyl anion. A similar conclusion is valid for antibonding MOs of a CA molecule.

Furthermore, of the six MOs of CA whose composition is similar to that of MOs of Cp^-, only three MOs can contribute considerably to bonding with MCp^+, since the energies of MOs having identical symmetry

Table 1. Results of EHM calculations of η^5-π-complexes of fullerene C_{60} and comparable systems (the parameters of EHM are given in Table 3)

System	Energy/eV				Overlap population/at. units		Charge/at. units	
	$-E_{\mathrm{overall}}$	$U(\mathrm{M-C_{60}})^a$	$U(\mathrm{M-L})^b$	δ^c	$\mathrm{M-C_{60}}$	M—L	q_M	q_L
C_{60}	4243.28	—	—	1.558	—	—	—	—
$FeCp^+$	538.88	—	—	1.814	—	0.780	0.14	0.86
$RuCp^+$	526.62	—	—	1.074	—	0.520	0.99	0.01
$OsCp^+$	532.02	—	—	1.418	—	0.305	0.54	0.46
$FeCp_2$	998.05	—	3.28	4.193	—	0.775	0.06	−0.03
$RuCp_2$	985.42	—	2.91	2.382	—	0.405	0.86	−0.43
$OsCp_2$	990.94	—	3.03	3.187	—	0.665	0.36	−0.18
$C_{60}—FeCp^+$	4784.51	2.35	—	1.317	0.645	0.795	0.22	0.07
$C_{60}—RuCp^+$	4772.26	2.36	—	0.725	0.280	0.430	1.01	−0.34
$C_{60}—OsCp^+$	4777.58	2.28	—	1.175	0.520	0.685	0.50	−0.08
Cp^-	455.89	—	—	5.174	—	—	—	—
Cp	443.90	—	—	0.000	—	—	—	—
C_{60}—CrBz	4852.60	6.11	6.99	0.218	0.665	0.768	−0.05	−0.25

[a] Energy of fragmentation $C_{60}ML \rightarrow C_{60} + ML$.

[b] Energy of fragmentation $CpMCp \rightarrow CpM^+ + Cp^-$ or $C_{60}ML \rightarrow C_{60}M + L$.

[c] $\delta = E_{\mathrm{HUMO}} - E_{\mathrm{LUMO}}$.

Table 2. Results of EHM calculations of η^6-π-complexes of fullerene C_{60} and comparable systems (the parameters of EHM are given in Table 3)

System	Energy/eV				Overlap population/at. units		Charge/at. units	
	$-E_{\text{overall}}$	$U(\text{M—C}_{60})^a$	$U(\text{M—L})^b$	δ^c	M—C_{60}	M—L	q_M	q_L
$C_{60}FeCp^+$	4783.36	1.20	—	1.516	0.480	0.800	0.56	0.13
$C_{60}CrBz$	4852.24	5.75	6.63	0.326	0.654	0.780	0.88	−0.13
$C_{60}MoBz$	4847.82	2.70	6.53	0.196	0.594	0.690	1.31	−0.14
$C_{60}WBz$	4847.56	3.06	6.79	0.150	0.708	0.798	2.09	−0.19
$C_{60}Cr$	4313.97	3.37	—	0.700	0.738	—	0.33	—
$C_{60}Mo$	4309.65	3.47	—	0.336	0.666	—	0.75	—
$C_{60}W$	4309.13	3.63	—	0.248	0.792	—	1.54	—
Bz_2Cr	1144.54	—	8.69	1.929	—	0.684	0.12	−0.06
Bz_2Mo	1139.76	—	6.28	1.592	—	0.636	0.18	−0.09
Bz_2W	1139.10	—	6.24	1.318	—	0.696	0.30	−0.15
BzCr	603.21	—	4.25	1.020	—	0.882	0.07	−0.07
BzMo	601.84	—	7.20	0.839	—	0.780	0.22	−0.22
BzW	601.22	—	7.36	0.903	—	0.858	0.34	−0.34
Bz	531.64	—	—	4.286	—	—	—	—

[a] Energy of fragmentation $C_{60}ML \rightarrow C_{60} + ML$.

[b] Energy of fragmentation $C_{60}ML \rightarrow C_{60}M + L$ or $BzMBz \rightarrow BzM + Bz$.

[c] $\delta = E_{\text{HOMO}} - E_{\text{LUMO}}$.

vary notably. Taking this and the less favorable conditions for overlapping of p-AOs of the CA molecule with the corresponding orbitals of a transition metal atom into account, we come to the conclusion that the probability of formation of π-complexes η^5-(CA)MCp$^+$ should be lower than that of analogous classical sandwich-type compounds.

This effect is even more pronounced in the case of fullerene C_{60}. In fact, due to higher delocalization, the coefficients at AOs of atoms located on a pentagonal face of the fullerene are smaller than those of CA. For example, in the case of MOs of C_{60}, which are completely symmetrical with respect to a five-order axis, the coefficients at the AOs of atoms of the respective five-membered cycle are at least four times smaller than the coefficients in a MO with symmetry a_1 for the cyclopentadienyl anion Cp^-. The situation with MO coefficients of fullerene hexagonal faces is similar.

Thus, a qualitative analysis shows that both η^5-π- and η^6-π-complexes of the fullerene are less stable than classical sandwich-type complexes involving cyclopentadienyl and benzene; furthermore, coordination at a pentagonal fullerene face is more energetically favorable than at a hexagonal face. These conclusions are in agreement with the results of semiquantitative calculations by the expanded Hückel method.

EHM calculations of fullerene η^5- and η^6-π-complexes

Tables 1 and 2 present energies of the bonds M—C_{60}, M—Cp, and M—(C_6H_6), their overlap populations, effective charges at the M atoms and at rings, overall energies and differences of LUMOs and HOMOs calculated by EHM. Table 3 contains the values of the parameters used in the calculations.

Table 3. Parameters used in EHM calculations

Atom	AO	$-H_{ii}$/eV	ζ_1	ζ_2	c_1	c_2	Ref.
H	1s	13.60	1.3	—	—	—	8
C	2s	21.40	1.625	—	—	—	8
	2p	11.40	1.625	—	—	—	
Cr	3d	11.22	4.95	1.60	0.4876	0.7205	8
	4s	8.66	1.70	—	—	—	
	4p	5.24	1.70	—	—	—	
Mo	4d	10.50	4.54	1.90	0.5899	0.5899	9
	5s	8.34	1.960	—	—	—	
	5p	5.24	1.920	—	—	—	
W	5d	10.37	4.98	2.068	0.6685	0.5424	9
	6s	8.26	2.341	—	—	—	
	6p	5.17	2.309	—	—	—	
Fe	3d	12.70	5.35	1.80	0.5366	0.6678	8
	4s	9.17	1.90	—	—	—	
	4p	5.37	1.90	—	—	—	
Ru	4d	11.12	5.378	2.303	0.5340	0.6365	10
	5s	8.60	2.078	—	—	—	
	5p	3.28	2.043	—	—	—	
Os	5d	11.84	5.55	2.416	0.6372	0.5598	10
	6s	8.17	2.45	—	—	—	
	6p	4.81	2.429	—	—	—	

Note. Off-diagonal matrix elements H_{ii} (in a two-exponent basis with exponents ζ_1, ζ_2 and coefficients c_1, c_2) were calculated by "weighted" formulas given in Ref. 7 at k = 1.75. The following distances (Å): r(M—Cp) = 1.66 (M = Fe), 1.84 (Ru), 1.86 (Os), and 1.80 (Cr); r(M—Bz) = 1.61(Cr), 1.79(Mo), 1.79(W), and 1.50 (Fe) and bond lengths (Å): r(C—C) = 1.42(Bz), r(C—C) =1.43 (Cp), r(C—H) = 1.09 were used.

The species MCp^+ (M = Fe, Ru, Os) and $M(C_6H_6)$ (M = Cr, Mo, W) chosen for studying fullerene interaction with organometallic moieties have three vacant MOs which predominantly consist of hybrid AOs of the corresponding metal atoms. As was mentioned above, these MOs mostly interact with three fullerene MOs of suitable symmetry and energy. It should be emphasized that this qualitative picture is similar for fullerene η^5- and η^6-π-complexes. The EHM calculations do not take electrostatic interactions into account in an explicit form. Therefore, to simplify a comparison of fragmentation energies (see *U*(M—L) in Table 1), the calculations in the case of classical sandwich-type structures CpMCp (M = Fe, Ru, Os) were performed for the heterolytic process:

$$U(\text{M—L}) = E(\text{Cp}^-) + E(\text{MCp}^+) - E(\text{CpMCp}).$$

It should also be noted that the EHM parameters taken[8—10] were originally used for solving significantly different problems not involving a comparison of compounds of different transition metals with each other. Therefore, our results are unlikely to explain changes in properties of the complexes dependent on the nature of the metal. However, the parameters used by us vary significantly, and conclusions which are not sensitive to these parameters seem to be sufficiently valid.

It is seen from Table 1 that in all cases the MCp^+ cation bonds to the cyclopentadienyl anion more strongly than with a fullerene pentagonal face in its η^5-π-complexes. Hence, the overlap population of a (M—five-membered ring) bond is larger than that of a (M—fullerene face) bond. As one could expect, this difference is especially pronounced when the bonds inside a fullerene η^5-π-complex are compared. It is also evident from Table 1 that the electron density "transfer" from the cyclopentadienyl anion to MCp^+ is greater than that from the fullerene.

The difference in the properties of coordination bonds of transition metal atoms with a conjugated hydrocarbon cycle, on the one hand, and a fullerene face, on the other hand, is even greater in the case of hexagons (in complete agreement with the qualitative analysis made above). As is evident from Table 2, the M—(C_6H_6) bond, both in classical sandwiches $(C_6H_6)_2M$ and in fullerene η^6-π-complexes, is much stronger than the M—C_{60} bond, and hence has a higher overlapping population. The charge distribution is more complex: there is not even approximate additivity on going from semi-sandwiches $(C_6H_6)M$ to sandwiches $(C_6H_6)M(C_6H_6)$. The explanation is that the dative component of the M—ring bond is much more pronounced in this case. Although each of the donor-acceptor and dative contributions changes in a regular manner, their competing action determines an unpredictable overall effect. This relates even more to fullerene η^6-π-complexes, in which the role of the dative components is much more significant.

We made a direct comparison of isomeric fullerene π-complexes, in which η^5- or η^6-coordination of the metal atom takes place, with $C_{60}FeCp^+$ and $C_{60}Cr(C_6H_6)$, respectively, as examples. In both cases, coordination of the metal atom at the pentagonal fullerene face is more energetically favorable, in complete agreement with the conclusions drawn from the qualitative analysis.

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