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Abstract

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THE ELECTRONIC STRUCTURE OF CHROMOCENE AND SOME OTHER RELATED COMPOUNDS

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In a previous paper ([1])* we calculated the molecular orbitals (M.O.) of dibenzenechromium, ferrocene, and the cobalticinium cation by the self-consistent M.O. method (the Roothaan method ([2])). According to the calculation, both in ferrocene and in dibenzenechromium there is a certain effective positive charge on the central atoms, so that the electrons are partially displaced from the neutral metal atom toward the aromatic rings. This result contradicts the views, adopted by some authors, that the decisive role in the stability of aromatic metal complexes is played by donor–acceptor bonds between pairs of π-electrons of the aromatic ligands and vacant orbitals of the central atom ([3]), since such bonds should lead to transfer of electrons from the rings to the metal atom. The electron-density distribution found by us indicates that in dibenzenechromium the reverse displacement of electrons, from the central atom to the rings, corresponding to the formation of dative-type bonds (at the expense of pairs of metal electrons and vacant antibonding orbitals of the rings), compensates and even exceeds the displacement due to donor–acceptor bonds. The positive charge on the metal atom in ferrocene proved to be smaller than in dibenzenechromium, since in the former molecule donor–acceptor bonds lead to a greater displacement of electrons from the rings to Fe, and this displacement can no longer be compensated by dative bonds and is outweighed only owing to the great polarity of bonds of the e_{1g} type (at the expense of the unpaired electrons of C_5H_5 and Fe), with displacement of electrons from Fe to the rings.

It appears to us that these results may be connected with the relative positions of the atomic orbitals of the central atom and the M.O.' s of the rings, since the conditions for interaction of A.O.' s and M.O.' s of the same symmetry depend on the difference in the energies of the corresponding orbitals. A rough idea of the positions of the A.O.' s can be obtained from atomic spectra. The corresponding diagrams for Fe and Cr are given in Fig. 1. As can be seen, the levels of the free Cr atom lie higher than the corresponding levels of the Fe atom. On the other hand, the a- and e-levels of the π-electrons of the C_6H_6 ring, both bonding and antibonding, lie deeper than the corresponding levels of the C_5H_5 ring (see Fig. 2). Therefore one may suppose that the conditions for interaction with formation of donor–acceptor bonds in dibenzenechromium are least favorable, since the occupied orbitals of C_6H_6 are situated deep, while

Fig. 1. Arrangement of the atomic electronic levels in Fe and Cr atoms (in eV)

Figure 1: Fig. 1. Arrangement of the atomic electronic levels in Fe and Cr atoms (in eV)

the vacant orbitals of Cr lie comparatively high and the corresponding bonds should probably be weak. Dative bonds, however, may be strong, since the occupied de_{2g}-orbitals of Cr and the vacant e_{2g}-orbitals of the rings may be close in energy (see Fig. 3). On the other hand, in the case of ferrocene, the distance between the lower-lying vacant A.O.' s of Fe and the higher

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* In our paper ([1]) an error was made: all values of dipole moments occurring in the table and in the text must be multiplied by 4.8.

π-orbitals of C_5H_5 should be smaller than in dibenzenechromium, so that an increased role of donor–acceptor bonds should be expected, whereas the conditions for dative interaction in ferrocene are less favorable. In connection with the foregoing, it is of interest to consider the chromocene molecule $(C_5H_5)_2Cr$, which has the same central atom as dibenzenechromium and the same ligands as ferrocene, and which should occupy an intermediate position between $(C_5H_5)_2Fe$ and $(C_6H_6)_2Cr$.

In the present work we have calculated the M.O.' s of chromocene by the Rüütan method in its generalized form for radicals ([4]) (since $(C_5H_5)_2Cr$

Fig. 1. Arrangement of the atomic electronic levels in Fe and Cr atoms (in eV)

has two unpaired electrons). In the calculation, simplifying assumptions were made analogous to those adopted in our preceding work ([1]).

Table 1

Symmetry	Bonding M.O.: orbital type	Bonding M.O.: energy, eV	Antibonding M.O.: energy, eV
a_{1g}	$0.97a_{1g} + 0.25s$	−13.71	+1.74
a'_{1g}	d_{z^2}	−4.82	–
a_{1u}	$0.99a_{1u} + 0.06p_z$	−13.12	+3.73
e_{1g}	$0.92e_{1g} + 0.39d_{xz}$	−10.56	+7.94
e_{1u}	$0.94e_{1u} + 0.35p_x$	−9.82	+4.05
e_{2g}	$0.55e_{2g} + 0.83d_{xy}$	−5.22	+5.88
e_{2u}	–	–	+4.00

The molecular orbitals of $(C_5H_5)_2Cr$ and their energies are given in Table 1. The ground state of $(C_5H_5)_2Cr$ has the form

$$(a_{1g})^2(a'_{1u})^2(e'_{1g})^4(e_{1u})^4(e_{2g})^3(a_{1g})^1. \qquad \text{(A)}$$

Another possible triplet state is

$$(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{1u})^4(a_{1g})^2(e_{2g})^2, \qquad (\ )$$

in which both unpaired electrons would be in the doubly degenerate e_{2g} level, lying above the a'_{1g} level occupied by a pair of electrons; this is refuted by the fact that for B it is not possible to obtain self-consistent M.O.'s. This conclusion regarding the ground state is in agreement with that previously reached by us in considering the valence states of chromium in chromocene ([5]). The calculated energies of the e_{2g} and a'_{1g} levels (respectively, -5.22 and -4.82 eV) proved to be close, so that in the immediate vicinity of the ground state there may be a diamagnetic state

$$(e_{2g})^4(a'_{1g})^0. \qquad (\ )$$

This shows that the observed paramagnetism of chromocene and the absence in it of an equilibrium between the para- and diamagnetic forms are due not to a significant difference in the energies of the upper occupied electronic levels, but to a difference in the energies of the initial valence states leading to the molecular states A and B (respectively, 128 and 187 kcal).

The latter conclusion applies not only to $(C_5H_5)_2Cr$, but apparently also to other aromatic complexes. In all the molecules we have considered, the upper occupied levels are levels of symmetry e_{2g} and a'_{1g}, these levels being close in energy. In $(C_5H_5)_2Fe$ and $(C_5H_5)_2Co^+$ the e_{2g} level lies above a'_{1g}, whereas in Cr compounds an inversion occurs (probably because of the greater role of dative bonds) and the e_{2g} level turns out to be below a'_{1g}. Apparently, in aromatic metal complexes the a_{1g} and e_{2g} levels are close to accidental degeneracy. Such a con-

C_5H_5	C_6H_6
e_2 — $C_1 - 1.618\,\beta$	$b - C_2 - 2\beta$
e_1 — $C_1 + 0.618\,\beta$	e_2 — $C_2 - \beta$
$a - C_1 + 2\beta$	e_1 — $C_2 + \beta$
	$a - C_2 + 2\beta$

Fig. 2. Arrangement of the π-electron levels according to the primitive MO-LCAO method in the rings C_5H_5 and C_6H_6 ($C_2 < C_1$)

clusion concerning the symmetry of the upper occupied levels and their quasi-degeneracy is confirmed by McConnell' s experimental data ([6]) on the electron paramagnetic resonance of vanadicene $(C_5H_5)_2V$, for which it was found

I	II
$4s(a_{1g})\,Cr \longrightarrow C_5H_5(a_{1g})$	$3d(t_{2g})\,Cr \longrightarrow C_5H_5(e_{2g})$
$4s(a_{1g})\,Fe \longrightarrow C_6H_6(a_{1g})$	$3d(t_{2g})\,Fe \longrightarrow C_6H_6(e_{2g})$

Fig. 3. Relative arrangement of orbitals participating in the formation of donor-acceptor bonds of type a_{1g} (I) and dative bonds of type e_{2g} (II)

that its three unpaired electrons are distributed over the levels $(e_{2g})^2$ and $(a'_{1g})^1$.*

The presence of three levels close in energy (two e_{2g} levels and the a'_{1g} level) should lead to the fact that, from the point of view of MO energies, the difference between states with different distributions of electrons over the a'_{1g} and e_{2g} levels should be small. This confirms the assumption we made earlier that the number of unpaired electrons in aromatic complexes is determined by the difference in energy of the initial valence states.

The ionization potential of chromocene (the energy of the upper occupied a'_{1g} level) is equal to 4.82 eV, which is 70% of the experimental value (6.90 eV).

* In Yamazaki' s work ([7]) on the calculation of $(C_5H_5)_2Fe$, the upper occupied level has symmetry e_{1u}. This seems unlikely to us in light of the results we obtained from the MO calculation, the valence states, and the experimental data on the paramagnetic resonance of vanadicene.

The coefficients of the AOs in the MOs of chromocene lead to the following charge distribution: +1.70 electron charge on the Cr atom and −0.17 on each C atom. The charge on the Cr atom thus proved to be considerably greater than on the Fe atom in $(C_5H_5)_2Fe$ (+0.68). This result is consistent with the substantial difference in the properties of ferrocene and chromocene. As is known from chemical data, $(C_5H_5)_2Cr$ differs strongly from typical covalent bis-cyclopentadienyl compounds, approaching ionic $Mn^{2+}(C_5H_5^-)_2$, as manifested in an instantaneous metathetic reaction with $FeCl_2$ (with formation of ferrocene in 70% yield), hydrolysis by acids, and electrical conductivity ([8]). The study of IR spectra ([9]) led to the same conclusion concerning the considerable ionic character of $(C_5H_5)_2Cr$ and its closeness to $(C_5H_5)_2Mn$. On the other hand, the charge on the Cr atom in $(C_5H_5)_2Cr$ is close to that found for $(C_6H_6)_2Cr$ (+1.47), in agreement with the small dipole moment of the mixed complex $(C_6H_6)Cr(C_5H_5)$ (between 0 and 0.4 D) ([10]). The closeness of the charges on Cr in the bis-cyclopentadienyl and dibenzene compounds and the noticeable ionic character of $(C_5H_5)_2Cr$ allow one to suggest that $(C_6H_6)_2Cr$ too must be a partially ionic molecule, in which the benzene rings play the role of anions

(similarly to the way in which they pass into an anionic state upon interaction with alkali metals).

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Note: Figure translations are in progress. See original paper for figures.