THE SELECTION OF THE ATOMIC ORBITALS PLAYING A DETERMINING ROLE IN THE GROUPS FORMING COMPLEXES

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For bonding of the complexes formed by the transition metals the electrons d of the central ion, as well as the outer electrons ($n = 2$) of the complex forming groups are responsible. By means of a half empiric version of the LCAO—MO method it was investigated which states of the electrons of the radicals mentioned above must be taken into account. It was found that the significance of the $2p\sigma$ orbitals is dominating, nevertheless, the $2p\pi$ orbitals cannot be neglected either. The $2s\sigma$ states are, however, of secondary importance.

§ 1. Introduction

The theory of the complexes with covalent bonds was found by PAULING [1] who assumed that the complexes are formed by the localization of the electrons of the radicals into the empty states of the central ion. On the basis of PAULING's suggested theory KIMBALL [2] elaborated all the combinations of atomic orbitals which have to be considered at the bond. WOLFSBERG and HELMHOLZ [3] already deal with some complex ions taking the atomic orbitals of the radicals into consideration, too. The latter authors use the most simple version of the LCAO—MO method and the occuring integrals are calculated from the ionization energies. This method has been used by other authors [4]—[7] too. In the following the methods of WOLFSBERG and HELMHOLZ will be employed. It will be attempted to establish which of the possible orbitals ($2s\sigma$, $2p\sigma$, $2p\pi$) are the dominating ones in the case of complexes of type $Me(CN)_6^{z-}$ ($Me = Mn^{3+}$, Fe^{3+}, Co^{3+}).

§ 2. The method of the calculation

The molecular orbitals (MO) of the complex are composed by the linear combinations (LC) of atomic orbitals (AO). The five $3d$, one $4s$ and three $4p$ orbitals of the central ion contribute to this LC. The radicals which turn with their C atoms towards the central ion in the complex contribute pro radical at most with the orbitals one $2s\sigma$, one $2p\sigma$ and two $2p\pi$ of the atomic orbitals of their C atom to the MO's of the complex. In each case

the symmetry O_h will be considered and the combinations of the AO's mentioned above belonging to each irreducible representation of the group O_h. Owing to the variation principle the best MO's can be determined by these basic functions. At the calculations the integrals

$$\int \Phi_i^* \Phi_j dt = \mathcal{G}_{ij}, \quad \int \Phi_i^* \mathbf{H} \Phi_i dt = \mathcal{H}_{ii}, \quad \int \Phi_i^* \mathbf{H} \Phi_j dt = \mathcal{H}_{ij} \qquad (1)$$

appear, where Φ_i is one of the basic functions mentioned and $\mathbf{H}$ the Hamiltonian of the problem. Among the integrals (1) $\mathcal{H}_{ii}$ are determined from the ionization energy of the corresponding atomic states and the $\mathcal{H}_{ij}$ are calculated by the formula of WOLFSBERG and HELMHOLZ

$$\mathcal{H}_{ij} = F \mathcal{G}_{ij} \frac{\mathcal{H}_{ii} + \mathcal{H}_{jj}}{2}. \qquad (2)$$

In this expression F means a correction parameter which was determined by the calculations concerning the complex of $Me = Cr^{3+}$ so that the empiric results are obtained in the best possible manner and the complexes mentioned in § 1 were calculated with the F values mentioned. The overlap integrals $\mathcal{G}_{ij}$ of the group were determined by means of a previously used approximation [7] assuming a uniform bond intervall $2,00 \text{ Å}$ between the central ion and the C atom of the radical.

With the procedure briefly described above three different calculations were carried out. In all three calculations the atomic orbitals mentioned were taken into account.

(a) Taking the three $2p$ orbitals of the atom C among the orbitals of the radicals into account we have altogether 27 orbitals. In the functional space of these 27 atomic orbitals the representation of the group O_h can be decomposed in form

$$\Gamma_{27} = 2A_{1g} + 2E_g + T_{1g} + 3T_{1u} + 2T_{2g} + T_{2u} \qquad (3)$$

(as regards denotation see $e.\,g.$ [8]). The calculations relating to $Me = Cr^{3+}$ show that acceptable results can be obtained if the parameter F has the following values

$$F = \begin{cases} 2{,}20 & \text{for } \sigma \text{ bond} \\ 2{,}65 & \text{for } \pi \text{ bond.} \end{cases} \qquad (4)$$

The transitions obtained in this manner are collected in cm^{-1} in the columns a of the Table.

(b) Among the orbitals of the C atoms of the radicals only taking the orbital $2p\sigma$ into account we have 15 atomic orbitals. The adequate representation of the O_h group in the 15-dimensional functional space can be decomposed in the form

$$\Gamma_{15} = 2A_{1g} + 2E_g + 2T_{1u} + T_{2g}. \qquad (5)$$

As in this case only σ bonds appear for the corresponding value of the parameter F in (2)

$$F = 2,20 \tag{6}$$

can be used. The number of the transitions obtained in this manner decreases and are summarized in the column b of the Table.

Table

Mn^{3+}				Fe^{3+}			
a	b	c	d	a	b	c	d
7340	9370		5600	7500		9130	5000
	12750	14840		16940	15200	18430	
16701		17440			19240	20880	
	25800	21530		23560		23740	
28000		30070	(27000)	24450	24450	24650	24000
29690		30630	30500	27430	28600	25240	(25000)
33160			(33000)	31710			(31000)
33400				36150			33000
37030	37030		(37000)	39210	39210		39000
44700	44700	40430	41000	46310			45500
46750	46750		46000				

Co^{3+}			
a	b	c	d
7580		7750	6340
		9080	
10890			
15010			
18500	18510		
24290		23740	
		25220	(25000)
31140		30170	
34530			32000
42120	42120		38500
46150	46150		50000

(c) Finally, the orbitals $2s\sigma$ and $2p\sigma$ of the C atoms of the radicals were considered. In this case we have 21 atomic orbitals. The corresponding 21-dimensional representations of the O_h group can be decomposed in the following form

$$\Gamma_{21} = 3A_{1g} + 3E_g + 3T_{1u} + T_{2g}. \tag{7}$$

Now again only the σ bonds play a role but they have now increased in number. For F a value below that of (6) must be taken. According to the calculations concerning $Me = Cr^{3+}$ the value

$$F = 1{,}50 \tag{8}$$

seems to be the best. The transitions yielded by these calculations are summarized in the columns c of the Table.

§ 3. Discussions

On the Table it can be seen that in the case of the results of the calculations (b) the transitions corresponding to middle wave numbers (about 30.000 cm^{-1}) are missing, whereas in the case of the results of the calculations (c) the transitions of the higher wave number (about 40.000 cm^{-1}) are lacking. Thus the neglecting of the $2p$ orbitals (calculation (b)) causes the elimination of the transition of middle wave number. If the orbitals $2s$ are taken into consideration (calculation (c)) the transitions of middle wave number appear again but the transitions of higher wave number are shifted from the measurable range. Column d of the Table contains the empiric data [9]. The values in brackets show the localization of the inflection points of the absorption curve, the rest of the data that of the maxima of the curve in cm^{-1}. Owing to the observations the complexes in the range 10.000—20.000 cm^{-1} are highly transparent, in spite of this in this range the occurrence of bonds cannot be experimentally ruled out.

Finally, it can be established that the best results are yielded by the calculations (a). Thus the $2s$ orbitals of the radicals are of secondary importance as compared with that of the $2p$ orbitals.

References

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ИССЛЕДОВАНИЯ ИГРАЮЩИХ ВАЖНУЮ РОЛЬ АТОМНЫХ ОРБИТ ЛИГАНДОВ КОМПЛЕКСНЫХ ИОНОВ

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Ковалентные связы комплексов переходных металлов образуются d-электронами центрального иона и внешними электронами лигандов. С помощью полуэмпирического метода МО-ЛКАО было исследовано, какие орбиты лигандов должны быть расчитаны. По расчетам $2p\sigma$-орбиты оказываются более важными, а $2p\pi$-орбиты также не могут быть оставлены вез внимания. Роли 2s-орбит не существенны.