

WOLFSBERG—HELMHOLTZ CALCULATIONS ON $[\text{Fe}(\text{phen})_3]^{2+}$ AND $[\text{Fe}(\text{phen}-(\text{OH})_2)_3]^{2+}$ COMPLEXES

By

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WOLFSBERG—HELMHOLTZ calculation has been performed for $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{phen}-(\text{OH})_2)_3]^{2+}$ complexes. The bond between the metal and the ring and the modification caused by the OH radicals built in have been studied in this approximation.

In this paper we attempt to move one step forward in understanding the electronic structure of $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{phen}-(\text{OH})_2)_3]^{2+}$. The molecules have significance in redox processes; $[\text{Fe}(\text{phen})_3]^{2+}$ is applicable as a redox indicator. During the past years a model, known as the extended HÜCKEL model, or the WOLFSBERG—HELMHOLTZ model [1] has been used to study the molecular orbitals of all electrons in large molecules. The molecules we are dealing with are complicated, so we must neglect a great number of orbitals, especially the σ orbitals of C atoms and the s orbitals of H atoms.

Method

We try to find the solution of the equation

$$H_{\text{eff}}\psi_j = \varepsilon_j\psi_j$$

where the MO-s ψ_j are expanded in the minimal system of atomic orbitals:

$$\psi_j = \sum_p \varphi_p c_{pj}$$

The MO energies ε_j and the coefficients c_{pj} are solutions of the equation

$$\mathbf{Hc} = \varepsilon\mathbf{Sc} \quad (1)$$

In Eq. (1) \mathbf{H} and \mathbf{S} are the matrices of the effective Hamiltonian and the so-called overlap matrix, with the matrix elements

$$H_{pq} = (\varphi_p, H_{\text{eff}}\varphi_q), \quad S_{pq} = (\varphi_p, \varphi_q),$$

respectively. Instead of the calculated values, WOLFSBERG and HELMHOLTZ [1] suggested to use the ionization potential values of the atomic orbitals φ_p of the free atom for the diagonal elements H_{pp} , and the values

$$\frac{1}{2}KS_{pq}(H_{pp} + H_{qq})$$

for the off-diagonal elements H_{pq} , where K is an appropriate interaction parameter.

We expand ψ_j in terms of five $3d$, one $4s$ and three $4p$ orbitals of the central ion and one $2s$, two $2p$ orbitals of N atoms, as well as of the $2p_z$ orbitals of C and O atoms.

Model and geometry

The $[\text{Fe}(\text{phen})_3]^{2+}$ complex ion is formed by a central Fe^{++} ion and by three phenantroline molecules (Fig. 1). The nitrogens of phenantroline molecules (A, B

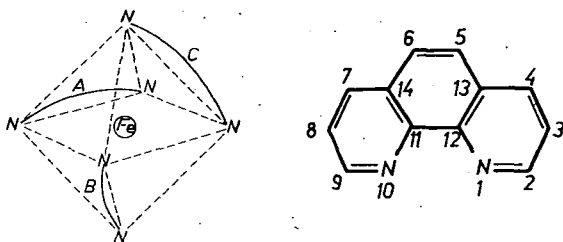


Fig. 1. Schematic structure of iron-phenantroline

and C) in position 1 and 10 occupy the vertices of the octahedra around the central ion. In the other ion, *i. e.* in the $[\text{Fe}(\text{phen}(\text{OH})_2)_3]^{2+}$ complex, the hydrogens bonded to C atoms in position 4 and 7 of the phenantroline molecules are substituted by OH radicals.

X-ray diffraction studies [2] led to a bond distance of 1.97 Å between metal and nitrogen. We assumed the C-C, C-N distances to be 1.39 Å, and the C-O distance 1.08 Å. Numerical calculations have been done by means of a MINSK-22 computer. In order to reduce computation time we have taken into account the symmetry properties of the molecules [3]. The symmetry group of molecules considered is D_3 .

Choice of parameters

For computing the overlap integrals we have used single orbitals of SLATER type:

$$\varphi(n, l, m) = N r^{n-1} \exp(-\zeta r) Y_l^m(\Theta, \Phi)$$

where N is a normalizing coefficient, n is the effective quantum number, which can be determined according SLATER's prescription and ζ is a parameter depending on the nuclear charge. CLEMENTI [4] proposed for ζ a higher value than that of SLATER. Computations by ZERNER and GOUTERMAN [5] for systems physically similar to our molecules have shown that a very satisfactory picture of the ligand field can be obtained by the following choice of ζ (Table I). These values of ζ lie between those given by SLATER and CLEMENTI. Using the parameter values of Table I, we have computed the overlap integrals shown in Table II.

Table I
Basis Set Exponentials*

	<i>s</i>	<i>p</i>	<i>d</i>
Fe	1.370	1.370	2.722
N	1.9237	1.9170	
C		1.5679	
O		1.2266	

* Ref. [5]

Table II
Overlap integrals

Overlap Type	(2 <i>s</i> , 4 <i>s</i>)	(2 <i>p_σ</i> , 4 <i>s</i>)	(2 <i>p_σ</i> , 3 <i>d_{z²}</i>)	(2 <i>s</i> , 3 <i>d_{x²-y²}</i>)	(2 <i>p_σ</i> , 3 <i>d_{x²-y²}</i>)
	0.38808	0.25276	0.03882	0.04903	0.06743
Overlap Type	(2 <i>s</i> , 3 <i>d_{z²}</i>)	(2 <i>p_z</i> , 3 <i>d_{xz}</i>)	(2 <i>p_π^C</i> , 2 <i>p_π^N</i>)	(2 <i>p_π^C</i> , 2 <i>p_π^O</i>)	(2 <i>p_π^C</i> , 2 <i>p_π^O</i>)
	0.02567	0.02682	0.2249	0.25102	0.2409

Table III
H_{pp} for Fe, N, C and O* Potential in eV

	<i>s</i>	<i>d</i>	<i>d</i>
Fe	$d^6 s^2 \rightarrow d^6 s - 7.90$	$d^6 sp \rightarrow d^6 s - 4.55$	$d^6 s^2 \rightarrow d^6 s^2 - 10.82$
N	$s^2 xyz \rightarrow sxyz - 25.17$	$s^2 xyz \rightarrow s^2 xy + (p) - 14.158$	
C		$s^2 xyz \rightarrow s^2 xy + (p) - 11.316$	
O		$s^2 x^2 yz \rightarrow s^2 xyz + (p) - 15.863$	

* Numbers in this table are from Ref. [8]

The ionization potentials of valence electrons of the free atoms used in the calculations are presented in Table III. HOFFMANN [6] proposed the value 1,75 for the interaction parameter, and we accept the same value for the π - π bond. For the H_{pq} values between central ion and nitrogen we used $K=1.89$ [5].

Results

The formation of metal-phenantroline bond mainly depends on the atoms of phenantroline. Comparing the obtained energies of orbitals (Tables IV and V), it can be seen that the substitution of OH radicals results in changes in the energies of the E orbitals.

By means of the components c_{pj} , obtained from the matrix equation, a so-called population analysis [7] has been performed. Results are presented in Tables VI and VII.

The π electron densities at the N atom are 1.3225 and 1.4081 in the first and second molecule, respectively. The electron density at O atoms is 1.7815, the values for C atoms are shown in Table VIII.

Table IV
Molecular-orbital energies of $[\text{Fe}(\text{phen})_3]^{3+}$ in eV

A_1	A_2	E	
-25.3341	-25.1618	-25.2342	-10.8936
-15.1388	-15.9441	-25.1613	-10.8183
-14.1521	-14.8581	-15.9928	-10.6337
-13.3673	-14.3211	-15.2817	-9.7981
-12.4468	-13.3619	-15.0711	-7.8781
-11.1087	-10.4607	-14.2339	-7.6562
-10.6681	-9.4342	-14.1611	-6.2707
-8.8528	-7.4593	-13.7598	-4.5182
-7.5032	-2.7258	-13.6096	-4.2295
-2.4381	-1.7348	-12.8571	-0.6301
-0.3861		-12.1058	

Table V
Molecular-orbital energies of $[\text{Fe}(\text{phen}(\text{-OH})_2)_3]^{2+}$ in eV

A_1	A_2	E	
-25.3341	-25.21618	-25.4491	-12.0464
-16.7525	-16.8557	-25.1638	-10.7329
-15.1349	-15.8484	-16.7668	-10.6108
-14.1521	-14.6166	-16.7652	-10.5605
-12.6964	-14.3211	-15.9927	-9.2405
-12.8428	-13.0487	-15.2458	-7.6264
-12.4212	-11.2148	-15.0678	-7.4691
-10.6868	-8.5651	-14.2533	-6.2054
-10.6681	-7.4574	-14.1613	-3.0532
-8.1227	-2.7258	-13.6141	-2.9192
-7.4796	-0.3384	-12.9563	-0.4106
-0.3861		-12.2662	

Table VI
Total electronic populations of $[\text{Fe}(\text{phen})_3]^{2+}$

Fe_2^+	$4s$	$4p$	$3d$	Total	Net
	0.453	0.0893	5.8074	6.3497	+0.3497
N	$2s$	$2p_\sigma$	$2p_\pi$		
	1.8653	1.8925	1.3235	5.0813	+0.0813

Table VII.

Total electronic populations of $[\text{Fe}(\text{phen}(\text{-OH})_2)_3]^{2+}$

Fe_2^+	4s	4p	3d	Total	Net
	0.453	0.0568	5.7437	6.2535	+0.2535
N	2s	2p _π	2p _π		
	1.8048	1.8719	1.4081	5.1848	+0.1848

Table VIII

 π electron densities of C' atoms

	C ₍₂₎	C ₍₃₎	C ₍₄₎	C ₍₅₎	C ₍₁₁₎	C ₍₁₃₎
$[\text{Fe}(\text{phen})_3]^{2+}$	1.0156	0.9566	0.9907	0.9793	1.0186	0.9713
$[\text{Fe}(\text{phen}(\text{-OH})_2)_3]^{2+}$	0.9944	1.0712	0.7168	1.0181	0.9634	0.9724

As it can be seen, the charge density at nitrogens is transferred to the π orbitals, a more intensive part in the bonds. 4s orbitals of Fe^{2+} have a considerable charge density in both cases. Substitution of the OH radicals is indicated by the changes in the charge density of the surrounding C atoms, as well as in the distribution of 3d and 4p orbitals of the Fe^{2+} ion.

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ВЫЧИСЛЕНИЕ ПО ВОЛФСБЕРГУ—ГЕЛЬМГОЛЬЦУ НА КОМПЛЕКСАХ
 $[\text{Fe}(\text{phen})_3]^{2+}$ и $[\text{Fe}(\text{phen}(\text{-OH})_2)_3]^{2+}$

Г. Пана

Мы провели вычисление по Волфсбергу—Гельмгольцу на комплексах $[\text{Fe}(\text{phen})_3]^{2+}$ и $[\text{Fe}(\text{phen}(\text{-OH})_2)_3]^{2+}$. При таком приближении исследовали связь между металлом и кольцами, и какие изменения дает в распределении электронов встроение радикалов OH.