IMPORTANCE OF π-BONDING IN THE STABILITY
OF THE IRON-GROUP CYANIDES

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ABSTRACT

Orthogonality conditions for M. O's are showed to imply an unique choice in calculating the energy levels of cyanide complexes using a two level problem corrected by a perturbation due to the third relevant level.

It is usually assumed in iron-group cyanides that the π and π^* levels play an essential role as far the electronic structure is concerned, via the so called "back-donation" effect [1].

In an energy scale, the metal t_{2g} levels lie between the π level and the higher level π^* of the ligand, but the overlap metal ligand level π^* is larger than the overlap metal-ligand π level [2]. Usually one constructs bonding orbitals with functions associated with maximum overlap, but in some cases energy considerations should also be taken into account, in order to satisfy stability conditions. The purpose of this note is to discuss how these stability conditions are connected to the orthogonality requirement of the M. O's. We call χ_1, χ_2 the orthogonal functions describing the π, π^* levels respectively, and φ the t_{2g} wave function of the metal ion. An independent linear combination of these functions read (normalization factors omitted).

$$\psi_1 = \chi_1 + \alpha_1 \varphi$$

$$\psi_2 = \varphi + \alpha_2 \chi_1 + \alpha_3 \chi_2 \qquad (1)$$

$$\psi_3 = \chi_2 + \alpha_4 \varphi$$

It is assumed that the M. O's satisfy the Schrodinger equation with a simplified Hartree-Fock hamiltonian h and that they are mutually orthogonal. In the following we adopt a perturbation approach to calculate the coefficients α_i and the energies, in the sense that one solves initially a two level pro-

blem, the effect of the remaining level being introduced as a correction.

We adopt first the assumption that the overlap criterion is the suitable one; this corresponds to put $S_1 = \langle \varphi | \chi_1 \rangle = 0$ and to solve the two level problem defined by:

$$\Phi_1 = \chi_1$$
$$\Phi_2 = \varphi + \alpha_3 \chi_2 \qquad (2)$$
$$\Phi_3 = \chi_2 + \alpha_4 \varphi$$

It is noted that (2) is deduced from (1) by imposing the orthogonality conditions between the M. O's and the assumption $S_1 = 0$. This corresponds, physically to ascribe to the π^* level an essential role in the bonding of the molecule. The solution of (2) are the well known results:

$$\alpha_3 = \frac{\langle \varphi | h | \chi_2 \rangle - S_2 \, \mathcal{E}_d}{\mathcal{E}_d - \mathcal{E}_{\pi^*}}$$

$$\alpha_4 = - \frac{\langle \chi_2 | h | \varphi \rangle - S_2 \, \mathcal{E}_{\pi^*}}{\mathcal{E}_d - \mathcal{E}_{\pi^*}} \qquad (3)$$

$$\mathcal{E}_1 = \mathcal{E}_\pi$$

$$\mathcal{E}_2 = \mathcal{E}_d - \alpha_3^2 \left[\mathcal{E}_{\pi^*} - \mathcal{E}_d \right]$$

$$\mathcal{E}_3 = \mathcal{E}_{\pi^*} + \alpha_4^2 \left[\mathcal{E}_{\pi^*} - \mathcal{E}_d \right]$$

where ε_d, ε_π, $\varepsilon_{\pi*}$, are given respectively by $\langle \varphi|h|\varphi \rangle$, $\langle \chi_1|h|\chi_1 \rangle$ and $\langle \chi_2|h|\chi_2 \rangle$, and it is assumed that $\varepsilon_{\pi*} > \varepsilon_d > \varepsilon_\pi$ as suggested by previous calculations [2].

It remains the question of the relative order of the energies ε_1. Using the results (3) it can be shown that $\varepsilon_2 < \varepsilon_1 < \varepsilon_3$ only if

$$\alpha_3^2 > \frac{\varepsilon_d - \varepsilon_\pi}{\varepsilon_{\pi*} - \varepsilon_d} \tag{4}$$

the other possibility implying that $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$.

We now show that the first possibility is not in fact allowed because it assumes that the overlap S_1, is rigorously zero. In fact let's introduce a small overlap S_1; this corresponds to introduce the following corrections in the functions Φ_1.

$$\psi_1 = \Phi_1 + \alpha_1 \varphi$$
$$\psi_2 = \Phi_2 + \alpha_2 \chi_1 \tag{5}$$
$$\psi_3 = \Phi_3$$

The orthogonality requirements imply that one should have:

$$\alpha_3^2 < \frac{\varepsilon_d - \varepsilon_\pi}{\varepsilon_{\pi*} - \varepsilon_d}$$

and this is in complete disagreement with the assumption (4) showing that the situation $\varepsilon_2 < \varepsilon_1 < \varepsilon_3$ is highly unstable.

The second possibility, $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$, although consistent with the orthogonality condition is also not physically satisfactory. In order to show this we start from (5) and calculate the corrections α_1 and α_2 within our perturbation scheme. One

finds:

$$\alpha_1 = \frac{\langle \varphi | h | \chi_1 \rangle - \varepsilon_1 S_1}{\varepsilon_1 - \varepsilon_d}$$

$$\alpha_2 = \frac{1}{\sqrt{N_2}} \frac{\langle \chi_1 | h | \Phi_2 \rangle - \varepsilon_2 S_1}{\varepsilon_2 - \varepsilon_\pi}$$

$$\varepsilon_1^{pert.} = \varepsilon_1 + \Delta\varepsilon_1$$

$$\varepsilon_2^{pert.} = \varepsilon_2 + \Delta\varepsilon_2$$

$$\Delta\varepsilon_1 = -\alpha_1^2(\varepsilon_d - \varepsilon_1)$$

$$\Delta\varepsilon_2 = \frac{1}{N_2} \frac{\left[\langle \chi_1 | h | \Phi_2 \rangle - \varepsilon_2 S_1\right]^2}{\varepsilon_2 - \varepsilon_\pi}$$

(6)

where N_2 is the normalization constant of Φ_2.

The effect of the small π admixture is then to introduce a bonding contribution to the ε_1 level ($\Delta\varepsilon_1 < 0$) and an antibond­ing contribution ($\Delta\varepsilon_2 > 0$) to the ε_2 level. The antibonding contribution to the ψ_2 orbital produces a decrease of the 10Dq parameter (if we assume as in 1 that the e_g^* states are qualitatively similar to these of an "ionic" complex). But this is in contradition to the experimental results, which show an increase respect to the "ionic" complexes. These results show that in spite of a larger overlap, energy considerations favour the choice of the π level in order to construct

the M. O's. If we adopt this choice, equation (2) is replaced by:

$$\Phi_1 = \chi_1 + \alpha_1 \varphi$$
$$\Phi_2 = \varphi + \alpha_2 \chi_1 \tag{7}$$
$$\Phi_3 = \chi_2$$

The solution of this two level problem together with the correction due to the χ_2 function reproduces results quoted [1], showing that the scheme adopted by Shulman and Sugano is the only one compatible with stability and the properties of the iron-group cyanides.

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REFERENCES:

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2. John J. Alexander and Harry B. Gray - Electronic Structures of Hexa-cyanometallate Complexes - Contribution № 3576 from Gates and Crellin Laboratories of Chemistry, California Institute of Technology.

ϕ_3 ψ_3

π^* X_2

φ_d

ϕ_2 ψ_2

ϕ_1 π X_1

ψ_1

$S_2 \neq 0$
$S_1 = 0$

$S_2 \neq 0$
$S_1 \neq 0$

ψ_3

ϕ_3 π^{*} X_2

φ_d

ϕ_2 ψ_2

π X_1

ψ_1

ϕ_1

$S_1 \neq 0$
$S_2 = 0$

$S_1 \neq 0$
$S_2 \neq 0$