Preliminary communication

MOLECULAR ORBITAL CALCULATIONS FOR f-ORBITAL COMPLEXES: THE DICYCLOOCTATETRAENYLCERIUM(III) ANION

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Summary

INDO SCF calculations on the title complex indicate that, although the single f-electron is essentially localised on the metal, the metal $5d$ (e_{1g} and e_{2g}) orbitals interact significantly with the ligands and play a major role in determining the total energy.

INDO type SCF-MO calculations [1—3] have proved to give a good description of the bonding in the $3d$ metallocenes and to show good accord with the ligand field treatment [4] of such species. Recently this latter approach was extended to the dicyclooctatetraenyl complexes of the lanthanides and actinides [5], in which some f-orbital—ligand interaction is thought to be involved, but the bonding scheme suggested could then only be based on a one-electron picture. It therefore seemed appropriate to adapt the INDO scheme to treat such f-orbital complexes, and as a first step we outline our results for the dicyclooctatetraenylcerium(III) anion.

Chemically this system behaves as a dominantly ionic, Ce^{3+} ($4f^1$) system, but unlike halo or oxo species, in which the metal H^{core} terms will lie well above the corresponding ligand quantities, the H_M and H_L terms will here be of comparable magnitude and the results will therefore be highly sensitive to the parameterisation used. We have therefore utilised this system to obtain a parameter scheme which will correctly reproduce the f^1 ground state and thus provide the basis for a general method for MO calculations on compounds of the early lanthanides.

The calculations were made using INDO type approximations [6] to the electronic Hamiltonian, considering $4f$, $5d$, and $6s$ orbitals as a basis set for cerium with the usual valence orbital set of $2s$ and $2p$ for the first row atoms. Orbital exponents for cerium were obtained by fitting a single exponential function to the numerical values of Herman and Skillman [7], whilst empirical

ionisation energies, electron affinities, and Slater—Condon F_k and G_k integrals were derived from spectroscopic data and will be discussed in more detail later. The parameters used are given in Table 1, and the F_0 terms were calculated theoretically assuming spherical charge distributions [6]. The neutral cerium atom configuration $4f^1 5d^1 6s^2$ was taken for the evaluation of the $U_{\mu\mu}$ terms. For the off-diagonal $H_{\mu\nu}$ terms the values of Pople [6] were used for the rings, whilst for the metal—ligand interactions the approximation $\beta = \frac{1}{2}(I_M + I_L)$ was adopted. The appropriate bond lengths were taken according to Hodgson and Raymond [8], but for simplicity the D_{8h} geometry was assumed.

Since the cerium atom positive charge is unknown and the $(I + A)$ values are moreover highly dependent thereon, we have treated these $(I + A)$ terms as parameters which may be varied within limits to reproduce the experimentally indicated $4f^1$ ground state. The results are however not very sensitive to changes in the orbital exponents. The calculated one-electron ordering using the parameters of Table 1 nevertheless implied complete filling of all the cerium f-orbitals, but on the basis of total energy, which includes the large two-electron γ_{df} and γ_{ff} terms, the single occupancy of the f-orbital set is found to be most favourable. Furthermore, raising the one-electron f-levels, so as to accord with semi-empirical calculations [5,9], yields $\pi^1_{e_{2u}}$ as the ground state on a total energy basis, whilst conversely a lowering of these levels gives rise to a $\pi^3_{e_{1g}}f^2$ electronic arrangement.

All the calculations indicated that the $4f$ orbitals were essentially localised, presumably due to their small overlaps with the ligands, whereas the $5d$ orbitals were extensively mixed into the formally ligand e_{1g} and e_{2g} molecular orbitals, the extent of this mixing being very sensitive to the choice of $(I + A)$ value. However, although the $5d_{z^2}$ and $6s$ orbitals (a_{1g}) are significantly mixed together, neither of these orbitals is involved to any great extent in the bonding. The $5d$ populations have though a marked effect in determining the total energy because of the large one-centre γ_{df} integrals.

The parameters of Table 1 correspond to $(I + A)$ terms appropriate for the formal charges $4f$ (+ 1.6), $5d$ (+ 0.4), and $6s$ (0.0), and lead to the energetic order $\pi^4_{e_{1g}} 4f^1 < \pi^4_{e_{1g}} \pi^1_{e_{2u}} < \pi^3_{e_{1g}} 4f^2$, with $E(\pi^4_{e_{1g}}\pi^1_{e_{2u}}) - E(\pi^4_{e_{1g}} 4f^1) = 1.6$ eV. With our present parameterisation the d-orbital admixtures are found to be 3, 27, and 29% for the a_{1g}, e_{1g}, and e_{2g} levels respectively, whilst the ionisation potentials for electron loss from the $4f^1$ and the $\pi_{e_{1g}}$ levels are found by total energy difference to be almost identical at a little over 3.5 eV. The overall one-electron splitting of the $4f$ orbitals is less than 500 cm^{-1} and we are currently extending our calculations in double precision to examine the

TABLE 1

PARAMETERISATION FOR THE DICYCLOOCTATETRAENYLCERIUM(III) ANION

	$\frac{1}{2}(I + A)$ (eV)	μ, orbital exponent
$4f$	19.10	3.65
$5d$	3.75	2.12
$6s$	3.23	1.40

influence of two-electron terms on this quantity and to investigate the related praeseodymium complex.

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