The Application of Simple Hückel Theory to Metal Trisacetylacetonates

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Summary Previous Hückel calculations applied to metal trisacetylacetonates are shown to be in error and are repeated and extended in the light of recent ionisation potential data, indicating that the approach is quantitatively inadequate for the present system.

SIMPLE Hückel theory has been employed by Barnum[1] to estimate the effect of metal–ligand (M–L) π-bonding on the electronic spectra[2] of a series of tervalent trisacetylacetonates, $\mathrm{M(acac)_3}$ (M = Ti, V, Cr, Mn, Fe, Co). Coulomb and exchange parameters were estimated from electronegativity and bond energy data, respectively, with the exception of the exchange parameter, β_{MO}, for the metal–oxygen π-interaction, which was left as a variable parameter. The original paper[1] should be consulted for background, method and notation. The treatment resulted in remarkably good correlations with the experimental band positions.

Important recent developments have been mass spectral investigations[4,5] of the trisacetylacetonates, in which the first appearance potentials of the $\mathrm{M(acac)_3^+}$ ions are identified with the ionisation potentials of $\mathrm{M(acac)_3}$ and compared with those predicted by the Barnum calculation and extensions[5] of the latter to Hacac, $\mathrm{Al(acac)_3}$ and complexes of closely related ligands. The calculations fail to reproduce even the qualitative trends of the mass spectral data (which are similar to those for the uncomplexed ligands) and it is suggested[5] that Koopmans' theorem may not apply to this system.

In the original calculation,[1] the eigenvalues for the functions of E symmetry were obtained by diagonalising the 6×6 energy matrix formed from the single given set of E-type symmetry orbitals. Unfortunately, however, this set of orbitals, ϕ, is not orthogonal to the two further sets, ϕ' and ϕ'', which are easily set down by cyclic permutation of basis functions. Thus, while correct doubly-degenerate eigenvalues might be obtained by diagonalising the 12×12 matrix formed from two of these linearly dependent sets, those obtained in the original paper are incorrect as terms off-diagonal with respect to the sets are omitted. The most straightforward step[6] to obtain proper orthogonal functions is to consider the two sets ϕ and $(\phi' - \phi'')$.

Suitable combinations of these can be taken, resulting in two new sets, one of which is symmetric, the other antisymmetric with respect to one of the C_2 axes. This transformation factorises the 12×12 matrix and one of the three possible sets of un-normalised orbitals is given in the Table.

TABLE

E-type symmetry orbitals for $\mathrm{M(acac)_3}$[a]

Symmetric w.r.t. C_2

$2d_{xy} - d_{xz} - d_{yz}$
$2\phi_{\mathrm{A}} - 2\phi_{\mathrm{E}} - \phi_{\mathrm{F}} + \phi_{\mathrm{J}} - \phi_{\mathrm{K}} + \phi_{\mathrm{O}}$
$2\phi_{\mathrm{B}} - 2\phi_{\mathrm{D}} - \phi_{\mathrm{G}} + \phi_{\mathrm{I}} - \phi_{\mathrm{L}} + \phi_{\mathrm{N}}$
$\phi_{\mathrm{H}} - \phi_{\mathrm{M}}$
$\phi_{\mathrm{G}} + \phi_{\mathrm{I}} - \phi_{\mathrm{L}} - \phi_{\mathrm{N}}$
$\phi_{\mathrm{F}} + \phi_{\mathrm{J}} - \phi_{\mathrm{K}} - \phi_{\mathrm{O}}$

Antisymmetric w.r.t. C_2

$d_{yz} - d_{xz}$
$2\phi_{\mathrm{A}} + 2\phi_{\mathrm{E}} - \phi_{\mathrm{F}} - \phi_{\mathrm{J}} - \phi_{\mathrm{K}} - \phi_{\mathrm{O}}$
$2\phi_{\mathrm{B}} + 2\phi_{\mathrm{D}} - \phi_{\mathrm{G}} - \phi_{\mathrm{I}} - \phi_{\mathrm{L}} - \phi_{\mathrm{N}}$
$2\phi_{\mathrm{C}} - \phi_{\mathrm{H}} - \phi_{\mathrm{M}}$
$\phi_{\mathrm{F}} - \phi_{\mathrm{J}} - \phi_{\mathrm{K}} + \phi_{\mathrm{O}}$
$\phi_{\mathrm{G}} - \phi_{\mathrm{I}} - \phi_{\mathrm{L}} + \phi_{\mathrm{N}}$

[a] For details of the notation, see ref. 1.

While the simple Hückel theory is much too approximate to be useful in interpreting detailed electronic spectra, it was plausible that the recent mass spectral data[4,5] might be more amenable to correlation with a simple one-electron energy level scheme and therefore the calculations were repeated. The values employed by Barnum for the parameters α_{C}, α_{O}, β_{CO} and β_{CC} were again used. As Forster's Hückel calculation on the acetylacetonate ion indicated that the results were sensitive to parameter choice, the values recommended by Streitwieser[8] (and used by Forster) were also used, and side-by-side comparisons of results using identical β_{MO} and α_{M} values made. Barnum's differential electronegativity correction formulae were followed. The problem was extended to two dimensions

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by variation of α_M, as well as β_{MO}. Barnum estimated his α_M values from neutral atom electronegativities and cited the Pauling electroneutrality principle as justification. It is now recognised[11,12] that this principle may not be obeyed as closely as previously thought. The valence state ionisation energy for the *d*-orbital of the free atom ground-state configuration of the individual metals[13] was used as an initial estimate of α_M, which was then systematically varied over a range of 30 kK. This range covered Barnum's values, but no ligand-field splitting corrections were included. The exchange parameter β_{MO} was again left as an adjustable parameter. The calculation procedure requires only the diagonalisation of a matrix.

For most values of α_M in the above range, a value of β_{MO} could be found which would fit the first appearance potentials of the mass spectra of the complexes to the highest occupied MO.‡ However, no consistent trend in the values of the parameters was apparent. There appears to be little advantage in tabulating specific examples of the calculations.

Despite the failure, one important conclusion of the original analysis[1] can be corroborated. Thus the interaction of the metal A_1 orbital with the lower, filled, bonding and higher, empty, antibonding ligand A_1 orbitals leaves its energy largely unchanged. This suppression of the effect of π-interaction (assuming it is significant) would show why the position of the acetylacetonate ion in the spectrochemical series indicates little or no π-antibonding effects.

While the simple MO picture may provide a reasonable pictorial description of the relative order of the occupied levels of highest energy in the ground states of these complexes,[3] the gross approximations inherent in the Hückel approach, plus the apparent non-applicability of Koopmans' theorem,[5] do not allow a more quantitative description of the properties considered here.

(*Received, May 5th,* 1969; *Com.* 628.)

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‡ Using octahedral group notation for convenience, the energies of the e_g orbitals were estimated (ref. 2) as energy less negative by a value Δ than those of the t_{2g} orbitals.

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