d-Orbital Energies in β-Ketoenolate Copper(II) Complexes

Michail A. Atanasov*

Institute of General and Inorganic Chemistry, Bulgarian Academy of Science, 1040 Sofia, Bulgaria

Michael A. Hitchman

Chemistry Department, University of Tasmania, Box 252C, Hobart, Tasmania 7001, Australia

Received February 26, 1993

The assignment of the electronic spectrum and ordering of the d-orbitals of $Cu(acac)_2$ and related complexes has long been the subject of controversy.[1-8] This is largely because the vibronic selection rules suggest that every d–d transition is allowed in each polarization, so that although single-crystal polarized spectra of several complexes have been recorded,[1-4,6] these provide little information on the band assignments. However, two new developments in the understanding of metal–ligand interactions which are relevant to $Cu(acac)_2$ type complexes have emerged recently. First, it has become apparent that in planar complexes such as these the $^2A_g(z^2)$ state occurs at very high energy, this effect generally being ascribed to configuration interaction between the copper $a_g(z^2)$ and $a_g(4s)$ orbitals.[9,10] Second, it has been recognized that for ligands such as acac the out-of-plane π-interaction should be described not by a single bonding parameter, as would conventionally be the case, but by two parameters representing the interaction with the in-phase and out-of-phase combinations of the ligand π-orbitals. This concept of "phase-coupled ligators" was incorporated into the angular overlap model (AOM) of the bonding in metal complexes by Ceulemans *et al.*,[11] who used it to explain the unusually large energy separation between the d_{xz}, d_{yz} orbitals in Co(II) Schiff base complexes.[12] These authors recognized that it is possible to predict the type of π-interaction which a conjugated ligand will produce using simple arguments based upon the number, occupancy, and symmetry of its π-orbitals, and these ideas were developed by Atanasov *et al.* in an interpretation of the electronic spectrum of $Cr(acac)_3$.[13] The application of the AOM to the bonding of conjugated bidentate ligands has been discussed in detail by Schäffer and Yamatera.[14] These groups all conclude that for the filled π-orbitals of acac the in-phase combination of oxygen orbitals, ψ, will be higher in energy than the out-of-phase combination, χ, and will thus be closer in energy to the metal d-orbitals, so causing a stronger antibonding interaction. This was indeed confirmed in an analysis of the luminescence of $Cr(acac)_3$.[15]

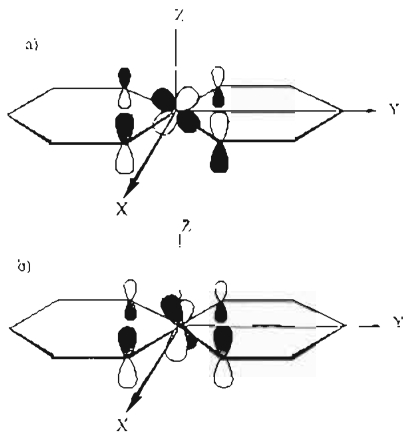

Figure 1. Schematic representation of (a) the in-phase combination of ligand π-orbitals, Ψ, and the d_{yz} metal orbital and (b) the out-of-phase combination of ligand π-orbitals, χ, and the Cu(II) d_{xz} orbital in $Cu(acac)_2$.

The present note considers the implications of the above developments on the assignment of the energy levels in $Cu(acac)_2$ type complexes, and the experimental data available for these systems, and its interpretation, is outlined below.

(1) The electronic spectra of single crystals of five compounds have been reported.[1-4,6] For $Cu(acac)_2$ itself,[1] three transitions are observed, at 14 500, 15 600, and 18 000 cm^{-1}, but for two other compounds all four d–d transitions are resolved.[2,6]

(2) The d–d spectrum of every complex is largely y polarized, where y bisects the chelate rings (Figure 1), and Belford *et al.* have suggested that this occurs because the intensity is mainly derived by vibronic coupling with a single, y polarized charge transfer transition.[2,4] Because of their temperature dependence, it was considered likely that the higher energy bands are to the $^2B_{3g}(yz)$ and $^2B_{2g}(xz)$ states, while the lower energy ones involve $^2A_g(z^2)$ and $^2A_g(x^2-y^2)$.

(3) The single-crystal electron paramagnetic resonance (EPR, sometimes labeled ESR) spectra of four $Cu(acac)_2$ type complexes have been reported.[3,16-18] and in every gase the g tensor is close to axially symmetric, suggesting that the $^2B_{3g}(yz)$ and $^2B_{2g}(xz)$ states are close in energy.

(4) Several studies of the optical spectra of adducts of $Cu(acac)_2$ and related complexes have been reported.[19] Amines produce square-based pyramidal adducts of C_{2v} symmetry showing an intense band at $\sim$16 000 cm^{-1}. Transitions to $^2B_2(yz)$ and $^2B_1(xz)$ are allowed in x and y polarization, respectively. The y spectrum of $Cu(acac)_2$·quin, quin = quinoline, shows a strong band at 16 400 cm^{-1} clearly due to the $^2B_1(xz)$ transition.[20] The $^2B_2(yz)$ state was tentatively assigned to the shoulder at $\sim$16 000 cm^{-1} in x polarization, but it seems probable that this is in fact due to the $^2B_1(xz)$ transition, the intensity coming from vibronic coupling. In view of the expected splitting of the $^2B_2(yz)$ and $^2B_1(xz)$ states, it seems more likely that the $^2B_2(yz)$ transition actually contributes to the band at 14 300 cm^{-1}, which is in fact the most intense peak in x polarization. The $^2A_1(x^2-y^2)$ transition then also contributes to the 14 300-cm^{-1} peak, with the band at 10 750 cm^{-1} being due to the $^2A_1(z^2)$ transition.

(5) The crystal structures of $Cu(acac)_2$·quin[21] and five $Cu(acac)_2$ type complexes have been reported.[3,22,23] The Cu–O bond

(1) Ferguson, J. *J. Chem. Phys.* **1961**, *34*, 1609.
(2) Belford, R. L.; Carmichael, J. W. *J. Chem. Phys.* **1967**, *46*, 4515.
(3) Hathaway, B. J.; Billing, D. E.; Dudley, R. J. *J. Chem. Soc. A* **1970**, 1420.
(4) Hitchman, M. A.; Belford, R. L. *Inorg. Chem.* **1971**, *10*, 984.
(5) Hitchman, M. A. *J. Chem. Soc. Faraday Trans. 2* **1972**, *68*, 846.
(6) Cotton, F. A.; Wise, J. *Inorg. Chem.* **1967**, *6*, 917.
(7) Nikolov, G. St.; Atanasov, M. A. *Inorg. Chim. Acta* **1983**, *72*, 95.
(8) Deeth, R. J.; Gerloch, M. *Inorg. Chem.* **1987**, *26*, 2578.
(9) Smith, D. W. *Inorg. Chim. Acta* **1977**, *22*, 107. Ceulemans, A.; Beyens, D.; Vanquickenborne, L. G. *Inorg. Chim. Acta* **1982**, *61*, 199.
(10) Gerloch, M.; Harding, M. J. H.; Woolley, R. G. *Struct. Bonding* **1981**, *46*, 1.
(11) Ceulemans, A.; Dendoven, M.; Vanquickenborne, L. G. *Inorg. Chem.* **1985**, *24*, 1153.
(12) Ceulemans, A.; Dendoven, M.; Vanquickenborne, L. G. *Inorg. Chem.* **1985**, *24*, 1159; Ceulemans, A.; Vanquickenborne, L. G. *Pure Appl. Chem.* **1990**, *62*, 1081.
(13) Atanasov, M. A.; Schönherr, T.; Schmidtke, H. *Theor. Chim. Acta.* **1987**, *71*, 59.
(14) Schäffer, C. E.; Yamatera, H. *Inorg. Chem.* **1991**, *30*, 2840.
(15) Atanasov, M. A.; Schönherr, T. *Inorg. Chem.* **1990**, *29*, 4545.
(16) Maki, A. H.; McGarvey, B. R. *J. Chem. Phys.* **1958**, *29*, 31.
(17) Hitchman, M. A.; Belford, R. L. *Electron Spin Resonance of Metal Chelates*; Yen, T. F., Ed.; Plenum Press: New York, 1969, p 69.
(18) Cotton, F. A.; Wise, J. *Inorg. Chem.* **1967**, *6*, 915.
(19) Belford, R. L.; Yeranos, W. A. *Mol. Phys.* **1965**, *6*, 121. Funck, L. L.; Ortolano, T. R. *Inorg. Chem.* **1968**, *7*, 567.
(20) Hitchman, M. A. *Inorg. Chem.* **1974**, *13*, 2218.
(21) Jose, P.; Ooi, S.; Fernando, Q. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1971.
(22) Robertson, I.; Truter, M. *J. Chem. Soc. A* **1967**, 309 and references therein.

0020-1669/93/1332-3973$04.00/0

lengths in the adduct are slightly longer than those in the planar complexes, and the OCuO angles in every complex are very close to 90°. In Cu(acac)$_2$·quin the Cu is raised out of the acac oxygen atom plane by 0.2 Å toward the amine nitrogen. The other complexes are centrosymmetric and effectively 4-coordinate, the closest axial contact being to the central carbon of the acac ring of another complex. Finally, the planes defined by the acac ligands in each complex are tilted by between 2 and 11° out of that formed by the Cu–O$_4$ atoms.

Assignment of the Optical Spectra. Assuming similar bonding characteristics for the range of complexes except for minor differences due to the above structural changes, only two general assignments of the optical spectra seem possible. This is because the spectrum of Cu(acac)$_2$·quin can be assigned unambiguously, certainly as far as the $^2B_1(xz)$ and $^2A_1(z^2)$ states are concerned, and the shorter Cu–O bond lengths, planarity of the Cu–O$_4$ grouping, and absence of significant axial ligation in the planar complexes all act to shift each d–d transition to higher energy compared with the adduct. For the planar complexes with four band spectra, the highest or second highest peak must therefore be to the $^2B_{2g}(xz)$ state, with $^2B_{3g}(yz)$ and $^2A_g(x^2-y^2)$ causing neighboring lower energy peaks.[24] The observed transition energies and possible assignments are shown in Table I for Cu(acac)$_2$·quin, Cu(acac)$_2$ itself, and Cu(3Ph-acac)$_2$; Cu(benzac)$_2$ has a three-band spectrum almost identical to that of Cu(acac)$_2$,[4] and Cu(dpm)$_2$ has a four-band spectrum similar to Cu(3Ph-acac)$_2$.[6] As the benzene group in 3Ph-acac is not conjugated with the acac π-system,[2] it should not affect the bonding characteristics significantly. The possible assignments differ largely in the energy of the $^2A_g(z^2)$ state. For the four-band spectrum, assignments I and II have this as the highest and lowest energy band, respectively. In the three-band spectrum, two transitions contribute to a single peak, and the $^2A_g(z^2)$ transition contributes to the highest band in assignment I and the lowest in assignment II.

Bonding Parameters of the Complexes. Neglecting the minor deviations of the OCuO bond angles from 90°, the AOM describes[9,14] the d-orbital energies E in the planar complexes by

$$E(xy) = 3e_\sigma;\ E(z^2) = e_\sigma - 4e_{ds};\ E(x^2-y^2) = 4e_{\pi c};\ E(xz) = 2e_\chi;\ E(yz) = 2e_\psi \quad (1)$$

Here, e_σ represents the σ-bonding interaction and e_{ds} the effect of d–s mixing.[9] The in-plane π-bonding is given by $e_{\pi c}$, and the out-of-plane π-bonding, usually described by the single parameter $e_{\pi s}$, is given by e_ψ and e_χ where ψ and χ designate interactions with the in-phase and out-of-phase combinations of the oxygen π-orbitals, respectively (Figure 1).[14] Each parameter refers to a single oxygen, rather than the ligand as a whole.

Equations 1 show that for the planar complexes the energy difference between $^2B_{2g}(xz)$ and $^2B_{3g}(yz)$ provides a direct measure of the relative interaction with the two symmetry combinations of the acac π-orbitals. For both assignments the band energies show that $e_\psi - e_\chi \approx 1000$ cm^{-1}. The sign of the splitting is that predicted theoretically,[11,13,14] while its size agrees quite well with the estimate of 1700 ± 300 cm^{-1} obtained[13] from the spectrum of Cr(acac)$_3$ considering that here the ligand field splitting is ~20% greater than that in the Cu(II) complexes.

Although the in-plane g-anisotropy of Cu(acac)$_2$ type complexes is always comparable to experimental uncertainty, for the three compounds where this was reported[3,16,17] g_x was in each case greater than g_y. The g-shifts from the free electron value may

Table I. Calculated and Observed Transition Energies (cm^{-1}) and AOM Bonding Parameters for Copper(II) β-Ketoenolate Complexes Compared with CaCuSi$_4$O$_{10}$

CaCu$_4$Si$_4$O$_{10}$			Cu(acac)$_2$·quin			Cu(acac)$_2$					Cu(3Ph-acac)$_2$				
							assignt I		assignt II			assignt I		assignt II	
E_{obs}	E_{calc}[a]	state[b]	E_{obs}	E_{calc}[a]	state[b]	E_{obs}	E_{calc}[a]	state[b]	E_{calc}[a]	state[b]	E_{obs}	E_{calc}[a]	state[b]	E_{calc}[a]	state[b]
12 740	12 700	$^2B_{2g}(xy)$	10 750	10 780	$^2A_1(z^2)$	14 500	14 440	$^2Ag(x^2-y^2)$	14 380	$^2Ag(z^2)$	15 400	15 360	$^2A_g(x^2-y^2)$	15 310	$^2Ag(z^2)$
16 130	{15 900	$2E_g(xz, yz)$	14 300	{13 800	$^2A_1(x^2-y^2)$	15 600	15 700	$^2B_{3g}(yz)$	{15 300	$^2Ag(x^2-y^2)$	16 900	16 910	$^2B_{3g}(yz)$	16 870	$^2Ag(x^2-y^2)$
	16 200}			14 500}	$^2B_2(yz)$	18 000	{17 550	$^2B_{2g}(xz)$	16 070}	$^2B_{3g}(yz)$	19 000	18 870	$^2B_{2g}(xz)$	19 090	$^2B_{3g}(yz)$
18 520	18 640	$^2A_{1g}(z^2)$	16 390	16 400	$^2B_1(xz)$		18 680}	$^2A_g(z^2)$	18 010	$^2B_{2g}(xz)$	20 600	20 530	$^2A_g(z^2)$	20 770	$^2B_{2g}(xz)$
$e_\sigma = 6500$			$e_\sigma = 6100$			$e_\sigma = 6500$			$e_\sigma = 6500$		$e_\sigma = 6900$			$e_\sigma = 6900$	
$e_\pi = 1700$			$e_{\pi c} = 1000$			$e_{\pi c} = 1250$			$e_{\pi c} = 1000$		$e_{\pi c} = 1325$			$e_{\pi c} = 950$	
$e_{ds} = 1325$			$e_\psi = 1600$			$e_\psi = 1900$			$e_\psi = 1600$		$e_\psi = 1900$			$e_\psi = 850$	
			$e_\chi = 750$			$e_\chi = 750$			$e_\chi = 850$		$e_\chi = 850$			$e_\chi = 50$	
			$e_\sigma(N) = 2000$			$e_{ds} = 1250$			$e_{ds} = 400$		$e_{ds} = 1600$			$e_{ds} = 400$	
			$e_{\pi s}(N) = 300$[c]												
			$e_{\pi c}(N) = 0$												
			$e_{ds} = 250$[c]												

[a] Calculated using the computer program CAMMAG with an effective spin-orbit coupling constant of 675 cm^{-1}; see text for reference from which experimental data were taken. [b] Designated according to the D_{4h} point group for CaCuSi$_4$O$_{10}$ and the D_{2h} or C_{2v} point group (Figure 1) for the remaining complexes. [c] Value only an approximation.

(23) Kirilova, N. I.; Strutchkov, J. T.; Martinenko, L. U.; Dzjubenko, N. G. *Metal β-diketonates*; Spizjin, V. I., Ed.; Nauka: Moscow, 1978 (in RUssian).
(24) See ref 20 for the reasoning behind this conclusion.

be related to the excited state energies by the expressions[25]

$$\delta g_x = -2k_x^2\lambda/^2B_{2g}(xz);\ \delta g_y = -2k_y^2\lambda/^2B_{3g}(yz);$$
$$\delta g_z = -8k_z^2\lambda/^2A_g(x^2-y^2) \quad (2)$$

As the $^2B_{2g}(xz)$ state is higher in energy than $^2B_{3g}(yz)$ for Cu(acac)$_2$ type complexes this should induce an in-plane *g*-anisotropy opposite to that observed. However, the anisotropy also depends on the orbital reduction parameters, and the observed sequence may be explained if $k_x > k_y$. For Cu(acac)$_2$ the *g*-values (g_x = 2.0551, g_y = 2.0519, g_z = 2.266) are reproduced by reduction parameters k_x = 0.757, k_y = 0.683, and k_z = 0.759 using assignment 1 of the observed transition energies as listed in Table I. Early studies interpreted *g*-values using molecular orbital coefficients,[26] but it has been suggested[27] that this is approach is oversimplistic. However, it seems reasonable that a stronger metal–ligand interaction will lead to a greater delocalization of the metal orbital and hence a smaller orbital reduction parameter. As the acac π-orbitals of ψ and χ symmetry interact with d_{yz} and d_{xz}, respectively, a stronger interaction involving the former implies that k_y should be smaller than k_x, as is indeed observed experimentally.

The bonding was studied more fully using the computer program CAMMAG developed by Gerloch and co-workers.[28] This calculates energy levels in terms of AOM bonding parameters using the observed geometry of the complex. Data on egyptian blue, $CaCuSi_4O_{10}$, were included for comparison. Here, the 4-coordinate Cu(II) is bonded to oxygen atoms in exact D_{4h} symmetry.[29] The optical spectrum has been assigned unambiguously,[30,31] and the calculated and observed transition energies are given in Table I, the former being obtained using the parameters e_σ = 6500, e_π = 1700, and e_{ds} = 1325 cm^{-1} (the distinction between ψ and χ symmetry combinations of π-orbitals is irrelevant here). The bonding parameters are similar to those of analogous compounds,[32] the ratio e_σ/e_π = 3.8 being that expected on the basis of the square of the diatomic overlap integrals,[33] and e_{ds}, which corresponds to a depression of 5300 cm^{-1} for $^2A_g(z^2)$, is close to values deduced for other planar complexes.[32] The calculated and observed transition energies of Cu(acac)$_2$, Cu(acac)$_2$·quin, and Cu(3Ph-acac)$_2$ are also given in Table I. Values of e_σ similar to that of $CaCuSi_4O_{10}$ were used in the calculations and the e_σ value used for the quinoline in Cu(acac)$_2$·quin was that found for this bond distance (2.36 Å) in a study of copper(II) amine complexes with differing axial coordination.[34] For the acac complexes, the bonding parameters are not unique, since in each case these outnumber the observed transition energies. However, the parameters are correlated (eq 1), so that raising e_σ by 200 cm^{-1} for each complex, for instance, requires an increase of $e_{\pi c}$, e_ψ, e_χ and e_{ds} by ~150, 300, 300, and −100 cm^{-1}, to produce the calculated transition energies in Table I.

The e_σ values follow the trend expected from the Cu–O bond lengths, these being similar in egyptian blue and Cu(acac)$_2$ (1.92 Å), slightly shorter in Cu(3Ph-acac)$_2$ (1.907 Å) and longer in Cu(acac)$_2$·quin (1.95 Å). Assignment I of the spectra of the planar complexes, which basically conforms to the d-orbital energy sequence proposed by Hathaway *et al.*,[3] leads to similar π-parameters for all three acac complexes, with e_ψ being similar to the e_π parameter of egyptian blue and e_χ being about half as large. This agrees with the proposal of Deeth and Gerloch[8] as far as the high energy of the $^2A_g(z^2)$ state is concerned, but differs in the assignment of the other states. These authors consider that the tilt of the acac rings out of the CuO_4 plane, see point (5) above, introduces a component of "bent bonding" to the metal–ligand interaction. This could possibly contribute to e_ψ in the present treatment, though no such effect was observed for Cr(acac)$_3$.[15] The in-plane π-bonding parameter $e_{\pi c}$ for the acac ligands is expected to be small, and may include contributions from "nonbonding" lone-pair electrons[35] and/or deviations of the ligand electron pairs from the Cu–O bond vectors.[8] The e_{ds} values agree well with those of other similar complexes.[32] The fact that e_{ds} is slightly smaller for Cu(acac)$_2$ than Cu(3Ph-acac)$_2$, 1250 cm^{-1} compared with 1600 cm^{-1}, is in line with the shorter distance between Cu and the central carbon of the ligands of neighboring molecules in the former compound (3.07 Å compared with the 3.5 Å).[22] Estimates of e_{ds} range from 1250–1875 cm^{-1} in other truly 4-coordinate planar complexes,[32] and it has been noted that in chlorocuprates, where data are available for a large range of axial Cu–Cl bond distances, the $^2A_g(z^2)$ state starts to become affected by axial ligation when the axial bond length drops below ~3.2 Å.[36] The main feature unexplained by this assignment is the intensity of the $^2B_{3g}(yz)$ transition in the planar complexes. It was suggested[20] that the band due to this transition is likely to be rather weak, as is indeed the case for Cu(acac)$_2$·quin, but assignment I requires it to be associated with a relatively intense band. Possibly the argument upon which this is based is too simplistic, depending as it does upon the assumption that the intensity is derived largely from a charge transfer state involving "lone-pair" ligand orbitals which are unable to overlap effectively with the metal d_{yz} orbital. Extended Hückel molecular orbital calculations by Cotton *et al.*[37] upon a model Cu(acac)$_2$ complex confirm the relative energies of the $^2B_{3g}(yz)$ and $^2B_{2g}(xz)$ states. We repeated these calculations using a computer program developed by Calzaferri[38] and obtained similar results. The possible influence of the carbon atoms of neighboring molecules upon the $^2A_g(z^2)$ state was also investigated, and it was confirmed that this is expected to be small.

Assignment II, which is basically that of Belford *et al.*[2,4] and Hitchman,[5] implies out-of-plane π-bonding parameters for the acac ligands which differ significantly among the complexes, which seems unlikely. Moreover, the low values it suggests for e_{ds} seem implausible. Ample evidence is now available that as a complex distorts from a regular octahedral to a square planar geometry, the $a_g(z^2)$ orbital lowers progressively in energy by $4e_{ds}$ = 5000–7000 cm^{-1},[32,34] and, as pointed out by Deeth and Gerloch,[8] the long axial interactions in the planar Cu(II) acac complexes seem inadequate to suppress a depression of this order of magnitude.

Acknowledgment. The financial assistance of the Humboldt Foundation (to M.A.A.) and the Australian Research Commission (to M.A.H.) is acknowledged, and Dr. M. Gerloch is thanked for making available the computer program CAMMAG. We are grateful to Professor G. Calzaferri (University of Bern) for the computer program used to carry out the molecular orbital calculations.

(25) Hitchman, M. A.; Olsen, C. D.; Belford, R. L. *J. Chem. Phys.* **1969**, *50*, 1195.
(26) McGarvey, B. R. *Transition Metal Chemistry*; Carlin, R. L., Ed.; Marcel Dekker: New York, 1966; Vol. 3, p 141.
(27) Smith, D. W. *J. Chem. Soc. A* **1970**, 3108.
(28) Gerloch, M. *Magnetism and Ligand Field Analysis*; Cambridge University Press: New York, 1983.
(29) Pabst, A. *Acta Crystallogr.* **1959**, *12*, 733.
(30) Ford, R. J.; Hitchman, M. A. *Inorg. Chim. Acta* **1979**, *33*, L167–L170.
(31) Mackey, D. J.; McMeecking, R. F.; Hitchman, M. A. *J. Chem. Soc., Dalton Trans.* **1979**, 299 and references therein.
(32) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; chapter 9.
(33) Smith, D. W. *J. Chem. Soc. A* **1970**, 1498.
(34) Deeth, R. J.; Gerloch, M. *Inorg. Chem.* **1984**, *23*, 3846.
(35) Deeth, R. J.; Duer, M. J.; Gerloch, M. *Inorg. Chem.* **1987**, *26*, 2573.
(36) McDonald, R. G.; Mitchman, M. A. *Inorg. Chem.* **1989**, *28*, 3996.33.
(37) Cotton, F. A.; Harris, C. B.; Wise, J. J. *Inorg. Chem.* **1967**, *6*, 909. Some errors occur in the tables in this paper; correct values may be found in: Wise, J. J. Ph.D. Thesis, MIT, 1965.
(38) Calzaferri, G.; Forss, L.; Kamber, I. *J. Phys. Chem.* **1989**, *93*, 5366. Calzaferri, G.; Brändle, M. Extended Hückel Calculations, ICONC & INPUTC. *QCPE Bull.* **1992**, *12* (4).