Impact on Ligand-field Theory of the Real Ground State for $CuCl_2$*

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The recent prediction by coupled pair functional Hartree–Fock calculations of a degenerate $^2\Pi_g$ ground term for linear $CuCl_2$ has been confirmed by local density functional (LDF) Slater-type orbital calculations. This has prompted a new cellular ligand field (CLF) analysis. Contrary to previous results on higher-co-ordinate chlorocuprates(II) and other complexes, the relative σ to π Cu–Cl bonding ratios for $CuCl_2$, as predicted by the CLF e_λ parameters on the one hand and by the LDF overlap populations on the other, do not agree. However, the CLF data do correlate with the computed LDF bonding energies but only when the whole d manifold (*i.e.* the $^2\Pi_g$, $^2\Sigma_g{}^+$ and $^2\Delta_g$ states) is taken into account. The interpretation and implications of these results within the ligand-field formalism are discussed.

Both ligand field (LF) and molecular orbital (MO) studies of transition-metal systems have, over the years, provided important insights into the nature of metal–ligand bonding. Within the LF formalism, the cellular ligand field (CLF) model of Gerloch and Woolley[1,2] has emerged as a useful approach.[3-8] On the all-electron side, treatments based on density functional theory (DFT) are rapidly establishing a reputation in transition-metal chemistry for speed and accuracy superior to conventional Hartree–Fock (HF) schemes.[9-12] All these approaches have similar goals and must be judged along similar lines. In the first instance, each method must reproduce experimental observables. Subsequently, it should then reveal details of the bonding in metal complexes.

It seems intuitively reasonable that either CLF of DFT calculations on the same compound or compounds should at least lead to comparable interpretations of the nature of the bonding. This view has, however, been challenged. It is argued[13] that one cannot expect agreement between electron-density-based descriptions (*i.e.* diffraction studies or all-electron computations using, say, DFT) and energy-level-based descriptions (*i.e.* LF theory). However, demanding that the bonding descriptions for the same compound should be at least qualitatively similar, irrespective of the method used, has in the case of $[Ni(NH_3)_4(NO_2)_2]$, revealed deficiencies in the interpretation of the experimental diffraction data.[14] The CLF treatment of this molecule[5] also needed revision and could only be made consistent with MO results (both HF and DFT) and the experimental diffraction data after explicit recognition of an hitherto unrecognised Ni–O(nitrite) interaction, this despite a Ni–O contact of some 3 Å.[14]

Other studies show a correlation between local σ and π bonding, as monitored by CLF e_λ values ($\lambda = \sigma, \pi_x$ or π_y), and the σ- and π-overlap populations derived from the DFT-based ground-state electron densities. A comparison[15] of CLF and local density functional (LDF) discrete variational Xα (DVXα) results on five chlorocuprates(II) of varying geometry and co-ordination number demonstrated that each model can reproduce the experimental d–d transition energies and with a similar ratio and variation of σ to π Cu–Cl bonding. However, at a detailed level, there was one discrepancy. In the CLF studies the local Cu–Cl perturbation is assumed to be cylindrically symmetric ($e_{\pi x} = e_{\pi y}$) yet the corresponding DVXα overlap populations in planar $[CuCl_4]^{2-}$ are not equivalent. At the time the difference was not considered significant. However, recent high-quality *ab initio* calculations[16] on linear $CuCl_2$ have prompted a reinvestigation of the source of this and related discrepancies.

Computational Details

All DFT calculations were based on the LDF program system due to Baerends *et al.*[17a] The method and some applications have recently been reviewed by Ziegler.[17b] The spin-unrestricted local density approximation[18] (LDA) was used in conjunction with analytical energy gradients[19] for all geometry optimisations. The LDA correlation energy was computed according to parameterisation of electron gas data by Vosko *et al.*[20] and includes Stoll's[21,22] correction for self-interaction. Subsequent total-energy calculations used to estimate electronic excitation energies included non-local exchange and correlation corrections as described by Becke[23] and Perdew[24,25] respectively. Geometry optimisations used Slater type orbital (STO) basis sets[26,27] of double ζ quality (triple ζ for the copper d orbitals) plus a 4p function for Cu. A 3d polarisation function on Cl was added for the calculation of total binding energies. The lower core shells on the atoms (up to 2p on Cu and Cl) were treated by the frozen-core approximation.[28] The total molecular electron density was fitted in each self-consistent field (SCF) cycle by auxiliary s, p, d, f and g STO functions.[29] Vibrational frequencies were estimated from second derivatives computed by finite differences of the first derivatives.

Results and Discussion

Bauschlicher's coupled pair functional (CPF) HF calculations on linear $CuCl_2$ predict the remarkable result of a $^2\Pi_g$ ground state.[16] This has important implications for the LF treatment of this apparently simple complex since other MO calculations[30,31] and all previous LF studies[32] have assumed a $^2\Sigma_g{}^+$ ground term. The CLF analysis of $CuCl_2$ is presented below. The CPF calculations are of high quality and include a good treatment of electron correlation and a comparison with the results from modern LDF methods is therefore of interest. The CPF data should be reliable but the $^2\Pi_g$ ground state is unexpected and warrants further verification.

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* *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

Table 1 Bond lengths (Å), electronic transition energies (cm^{-1}) and vibrational frequencies (cm^{-1}) for $CuCl_2$

	LDF–STO	CPF–HF	Exptl.
Cu–Cl($^2\Pi_g$)	2.065	2.056	—
Cu–Cl($^2\Sigma_g$)	2.090	2.091	—
Cu–Cl($^2\Delta_g$)	2.095	2.108	—
$\Delta E(^2\Sigma_g{}^+ - {}^2\Pi_g)$	5 574	659	*
$\Delta E(^2\Delta_g - {}^2\Pi_g)$	21 447	7 432	*
ν_{sym}	333	358	360
ν_{asym}	475	499	496
ν_{bend}	26	101	127

* Electronic absorption bands are observed at 9 000 and 19 000 cm^{-1} but an unambiguous experimental assignment cannot be given.

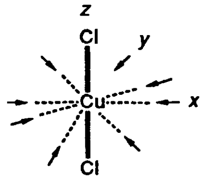

Fig. 1 Void cells for linear $CuCl_2$. The arrows indicate the positioning at 45° intervals of dummy ligands which represent the CLF void-cell contributions in the xy plane

Local Density Functional Results.—The quality of the LDF and CPF wavefunctions is comparable as measured by the ground-state vibrational stretching frequencies plus the energies and optimum bond lengths for the $^2\Pi_g$, $^2\Sigma_g{}^+$ and $^2\Delta_g$ states. The need for f functions on Cu in the CPF treatment does not appear to carry over to the LDF results. The theoretical data are compared with the available experimental data from ref. 16 in Table 1. The CPF and LDF bond lengths agree very well. The CPF vibrational stretching frequencies reproduce experiment exactly while the LDF results are systematically about 30 cm^{-1} too low. The LDF bending frequency is, however, relatively poor. This appears to be due to the use of finite difference methods for the estimation of second derivatives which, for the bending vibration of linear $CuCl_2$, leads to a change in the ground-state orbital degeneracy.

The excited-state energies, computed using the non-local corrected functional at the optimised ground-state geometry, give somewhat different assignments of the d–d transitions. The CPF data, which include spin–orbit coupling contributions, suggest the first experimental band, found at about 9 000 cm^{-1}, is d–d in origin with the second band, at about 19 000 cm^{-1}, being a charge–transfer (c.t.) excitation. The other d–d transition is predicted to lie below the lower limit of the instrumentation. The LDF results, which ignore spin–orbit coupling, indicate that both experimental absorptions could be d–d in origin. The omission of spin–orbit coupling should not be serious for the calculation of transition energies as the free-ion spin–orbit coupling constant for Cu^{II} is only about 830 cm^{-1} while the differences between the CPF and LDF results are of the order of several thousand cm^{-1}.

However, the LDF data also predict three additional transitions in the range 16 000–23 000 cm^{-1} apparently not considered by Bauschlicher. These c.t. bands occur at 16 607, 20 531 and 23 130 cm^{-1} arising from excitations from the $1\pi_u$, $2\sigma_u$ and $1\pi_g$ MOs respectively. The next c.t. transition occurs at 32 075 cm^{-1}.

An unequivocal assignment based solely on experimental evidence or on the theoretical results cannot be made since the available LDF code has no facility for computing oscillator strengths. Nevertheless, the disagreement over the calculated absolute energies of the excited states is of secondary importance with respect to the CLF treatment of $CuCl_2$ since the relative energies are the same for both theoretical models. The more contentious issue of an orbitally degenerate $^2\Pi_g$ ground state is confirmed.

It is noteworthy that single-determinant Hartree–Fock SCF theory gives the apparently intuitively reasonable but incorrect $^2\Sigma_g{}^+$ ground state for $CuCl_2$. The sophisticated but compute-intensive CPF treatment[16] corrects this error and gives impressive agreement with experiment but so too do the present LDF results and at a reduced computational cost.

Cellular Ligand Field Analysis.—Within the CLF formalism the whole xy plane of a linear system represents a large, annular 'void cell'.[33] In planar $[CuCl_4]^{2-}$, for example, these void cells lie along the z axis above and below the molecular plane and are each treated by a single e_σ parameter which takes a value of some −3000 cm^{-1}. For a linear system, the $D_{\infty h}$ symmetry can be maintained by modelling the void by eight separate 'ligands' lying in the xy plane at 45° intervals (Fig. 1). Within such a scheme, the d-orbital energies are given by equations (1a)–(1c).

$$E(d_{z^2}) = 2e_\sigma(\mathrm{Cl}) + 2e_\sigma(\mathrm{void}) \qquad (1a)$$

$$E(d_{x^2-y^2}) = E(d_{xy}) = 3e_\sigma(\mathrm{void}) \qquad (1b)$$

$$E(d_{xz}) = E(d_{yz}) = 2e_\pi(\mathrm{Cl}) \qquad (1c)$$

The relevant d–d transition energies become (2a) and (2b). With

$$E(^2\Pi_g \longrightarrow {}^2\Sigma_g{}^+) = E(d_{xz}) - E(d_{z^2}) = 2e_\pi(\mathrm{Cl}) - 2e_\sigma(\mathrm{Cl}) - 2e_\sigma(\mathrm{void}) \qquad (2a)$$

$$E(^2\Pi_g \longrightarrow {}^2\Delta_g) = E(d_{xz}) - E(d_{xy}) = 2e_\pi(\mathrm{Cl}) - 3e_\sigma(\mathrm{void}) \qquad (2b)$$

three CLF parameters to fit and only two possible d–d transitions, the CLF treatment is underdetermined. In previous CLF studies, recourse has been made to the so-called sum rule[34–36] wherein for similar complexes the sum, Σ, of all the diagonal e_λ values remains essentially constant. In practice, if the value of Σ is known, this will fix one degree of freedom. For four-, five- and six-co-ordinate chlorocuprates(II), the empirical value for Σ is between 24 000 and 26 000 cm^{-1}.[4] Whether this range is also valid for $CuCl_2$ may be debatable, but in any event the essential qualitative features of the CLF analysis presented below are largely independent of the precise value chosen for Σ.

The CLF parameter values for $CuCl_2$ can be determined by holding e_σ(void) fixed at some notional value and computing values for e_σ(Cl) and e_π(Cl) by fitting to the experimental transition energies. As discussed above, absorption bands are observed[37] at about 9000 and 19 000 cm^{-1} but there remains some controversy over their assignment.[32] Bauschlicher's calculations indicate the higher-energy band to be c.t. in origin suggesting assignment I for the d–d transitions: $^2\Pi_g \longrightarrow {}^2\Sigma_g{}^+$ at 1500 cm^{-1}; $^2\Pi_g \longrightarrow {}^2\Delta_g$ at 9000 cm^{-1}. The LDF–STO results, on the other hand, imply that the both the $^2\Sigma_g{}^+$ and $^2\Delta_g$ states are mainly of d-orbital character, leading to the d–d band assignment II: $^2\Pi_g \longrightarrow {}^2\Sigma_g{}^+$ at 9000 cm^{-1}; $^2\Pi_g \longrightarrow {}^2\Delta_g$ at 19 000 cm^{-1}. The results of representative CLF calculations using both assignments together with zero and negative values for e_σ(void) are collected in Table 2. The outstanding result to emerge from these data is the relationship $e_\pi(\mathrm{Cl}) > e_\sigma(\mathrm{Cl})$. For all other metal–chloride interactions so far examined the reverse trend is observed. For higher co-ordination numbers, $e_\sigma(\mathrm{Cl}) \approx 4e_\pi(\mathrm{Cl})$ but there the CuCl contact is about 0.2 Å longer than for $CuCl_2$. Perhaps the shorter bond length induces a significant enhancement of the chloride π bonding such that $e_\pi(\mathrm{Cl}) > e_\sigma(\mathrm{Cl})$, but this result would also presumably be manifest in the all-electron results.

Bauschlicher does not give a detailed analysis of the electronic distributions in $CuCl_2$ so all the following discussion is based on the present LDF calculations. Previously,[15] CLF parameter values have been correlated with LDF overlap populations derived from the ground-state electron density. The overlaps for the three essentially d–d states are collected in Table 3. Irrespective of the state there is a very poor correlation. The overlaps suggest the familiar $\sigma > \pi$ role for Cl^-. Evidently, in this instance Figgis[13] is correct in his assertion that no correlation is expected from the results of methods which deal directly with the electron density with those which model densities indirectly by examining the molecular energy levels.

Yet, the CLF scheme has been shown repeatedly[1–8] to provide a consistent description of metal–ligand bonding and molecular electron-density distributions. Does this imply that the CLF model fails for linear $CuCl_2$? Further light is shed on this question by analysing the energy contributions to the bonding derived from the LDF calculations.

LDF Bonding Energy Analysis.—The scheme developed by Ziegler *et al.*[38,39] decomposes the total bonding energy into two parts. The first describes the Pauli repulsion arising from bringing the separated parts of the molecule from infinity up to their bonding positions. This term accounts for the steric interaction arising from putting the constituent charge clouds together but without allowing them to overlap. The second part then describes the subsequent orbital interactions (overlaps) and hence models the bond covalency. This latter term can be conveniently broken down by symmetry so that theoretical estimates of individual σ- and π-bonding interaction energies can be extracted and compared directly with the CLF e_λ values.

Table 2 Cellular ligand field calculations on $CuCl_2$[a]

Assignment[b]	e_σ(Cl)	e_π(Cl)	e_σ(void)	Σ	e_π(Cl)/e_σ(Cl)
I	3 750	4 500	0	25 500	1.2
I	3 600	4 050	−300	21 000	1.1
II	5 000	9 500	0	48 000	1.9
II	4 250	7 250	−1 500	25 500	1.7

[a] All parameters in cm^{-1}. [b] See text for definitions of assignment schemes.

Table 3 The LDF–STO overlap populations for $CuCl_2$; Cu–Cl bond length fixed as 2.065 Å

Orbital	$^2\Pi_g$	$^2\Sigma_g{}^+$	$^2\Delta_g$	Whole manifold
σ_g	0.285	0.242	0.292	0.819
σ_u	0.151	0.172	0.187	0.508
π_g	0.064	0.020	0.044	0.128
π_u	0.116	0.154	0.182	0.452
Total σ	0.436	0.414	0.479	1.328
Total π	0.180	0.174	0.226	0.580
σ/π	2.42	2.38	2.12	2.29

The relevant energy terms are collected in Table 4. Again, there seems to be a poor correlation between CLF and LDF theories at least for the ground state. The total σ-orbital energy (−0.35 eV) is nearly twice the total π-orbital energy (−0.20 eV). However, the picture changes radically for the excited states. For $^2\Sigma_g{}^+$ and $^2\Delta_g$ the π-bonding energy exceeds the σ-bonding contribution. If the total picture arising from all the d states is examined (last two columns of Table 4) the π-orbital energy is actually greater than the σ-orbital value. Hence, on average, the CLF and LDF descriptions of the Cu–Cl energetic interactions are the same.

Implications for Ligand Field Theory.—This apparently anomalous result is consistent with the ligand-field formalism.[1] The solution of the many-electron Schrödinger equation is projected onto a basis set of pure d orbitals. The energy, E_i, of any particular state, Ψ_i, which is an eigenstate of the full Hamiltonian $\hat{H}$, can, as a matter of formal mathematics, always be expressed in terms of a projected basis, φ_i, and an effective Hamiltonian, $\hat{h}$, as in equation (3). This procedure demands that φ_i and $\hat{h}$ are defined concomitantly. In principle a different

$$\frac{\langle\Psi_i|\hat{H}|\Psi_i\rangle}{\langle\Psi_i|\Psi_i\rangle} = E_i = \frac{\langle\varphi_i|\hat{h}|\varphi_i\rangle}{\langle\varphi_i|\varphi_i\rangle} \qquad (3)$$

choice of φ_i and $\hat{h}$ is required for each different energy state but, in practice, a limited number of states, associated with those composed mainly of the d orbitals, are satisfactorily treated using a single set of functions (with orbital angular momentum $\ell = 2$) and a single operator (the LF Hamiltonian). Hence, a single set of LF parameters can reproduce the relative energies of those levels associated with the d–d transitions. Furthermore, reproduction of d–d assignments and magnetic properties implies that the detailed composition of these levels is also faithfully computed.

This single set of CLF parameters therefore describes the d-electron interactions with the remaining electrons not only in the ground state but in the excited d states as well. In contrast, the all-electron LDF model treats each state explicitly and independently. The bonding analysis for all states can be identical only when the d-orbital interactions with the other electrons remain constant across all the d states. This can only be rigorously true for spherical symmetry. In real molecules the orbital interactions differ from state to state, reflecting the differing bonding roles of the underlying functions. The so-called 'differential covalency' gives rise to the aspherical part of the LF potential which determines the values of the CLF parameters. Providing the variations are relatively small the

Table 4 The LDF–STO interaction energies (eV). Totals for σ and π in parentheses; Cu–Cl bond fixed at 2.065 Å

	State			
Contribution	$^2\Pi_g$	$^2\Sigma_g{}^+$	$^2\Delta_g$	Average
Steric	0.245	0.227	0.224	0.233
Orbital				
σ_g	−0.215	0.056	−0.179	−0.103
σ_u	−0.133 (−0.348)	−0.133 (−0.077)	−0.134 (−0.313)	−0.133 (−0.236)
π_g	0.020	−0.206	−0.201	−0.124
π_u	−0.222 (−0.202)	−0.218 (−0.202)	−0.217 (−0.418)	−0.218 (−0.342)
δ_g	0.005	0.005	0.303	0.106
Total	−0.547	−0.499	−0.430	
Total steric + orbital				
Uncorrected	−0.302	−0.272	−0.206	
Corrected *	−0.267	−0.243	−0.175	

* Becke[23] and Perdew[24,25] non-local corrections included.

description of the bonding derived from both CLF and LDF models will be qualitatively the same.

The case for small differential covalency has been put by Gerloch *et al.*[1] They argue that the ability of one parameter set to reproduce all the d-orbital-based energies implies a relatively constant radial extent for all the d orbitals. This assumption would fail if differential covalency were large unless each d function were involved in the bonding to about the same extent, thus keeping the differential covalency constant. This seems unreasonable, especially if the σ and π bonding from a particular ligand are very different, and therefore provides circumstantial evidence for the opposite conclusion that there is a relatively small differential covalency and hence weak d-orbital involvement in the bonding of Werner-type transition-metal complexes.[1]

The all-electron LDF calculations predict significant d-orbital covalency even in relatively ionic systems like metal halides,[15] yet the differential covalency is modest and the conclusions drawn from the LDF overlap populations correlate well with the CLF parameter values. For $CuCl_2$, however, the d-orbital contributions in the σ, π and δ MOs are about 55, 69 and 100% respectively. Under such extreme conditions, an analysis of the LDF ground-state electron density correlates poorly with the CLF e_λ parameter values. The LDF calculations indicate that σ bonding is more important in the ground state while the CLF parameters favour π bonding. The latter result is an artefact.

The source of the $\pi > \sigma$ picture emerging from the CLF analysis of $CuCl_2$ is revealed by the LDF energy decomposition. The CLF parameters reflect the averaged interaction over the whole manifold of d states. When all the LDF orbital interactions are considered the relative strengths of the σ and π interactions concur with the CLF data. In the apparently simple but extreme case of linear $CuCl_2$, the ground-state bonding interactions are very different from the average. The CLF treatment therefore incorrectly predicts a greater Cu–Cl π interaction relative to the σ interaction. Previous CLF analyses have concentrated on less-asymmetric systems where the differential covalency is reduced. The 'average' interactions are thus not too dissimilar from the ground-state values and a good correlation between ligand-field and all-electron methods is observed.

Conclusion

The LDF–STO calculations have confirmed the $^2\Pi_g$ ground state for linear $CuCl_2$ predicted recently by the more compute-intensive Hartree–Fock coupled pair functional method. Optimum bond lengths and infrared stretching frequencies also agree well both with the CPF results and with experiment. The LDF bending frequency is much poorer. The CLF calculations predict a greater Cu–Cl π interaction than σ, while an analysis of the LDF overlap populations gives the opposite result, $\sigma > \pi$. The source of this apparent anomaly can be traced to the underlying LF formalism. The CLF parameters are determined by fitting to experimental d–d transition energies and therefore monitor the (average) interactions between the d and the remaining electrons across the whole manifold of d states. The CLF prediction of $\pi > \sigma$ is seen in the LDF bonding energies but only when they are averaged over the whole manifold of d states. If, as here, the differential covalency becomes significant, the average picture is not the same as the ground-state picture. In such extreme cases, ligand-field theory can lead to erroneous conclusions concerning the metal–ligand bonding since this is a function of the ground state while the LF formalism describes an average over ground and excited states.

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