Discrete Variational Xα Calculations of the Spectra of Chlorocuprate(II) Complexes: A Detailed Comparison with Experiment and the Cellular Ligand Field Model *

Robert J. Deeth
School of Chemistry, University of Bath, Claverton Down, Bath BA7 2AY

Discrete variational Xα self-consistent-charge (DVXα s.c.c.) calculations of the *d–d* and charge-transfer (c.t.) spectra of five chlorocuprate(II) complexes have been performed. The molecules studied are planar and distorted tetrahedral $CuCl_4^{2-}$, square-pyramidal $CuCl_5^{3-}$, and two tetragonal-octahedral $CuCl_6^{4-}$ species. Calculated orbital-energy differences using near-minimal basis sets optimised for each molecule are in excellent agreement with experiment for the *d–d* bands. Transition-state calculations for the c.t. absorptions predict higher energies than observed but the energy differences between successive bands are well reproduced also. Analysis of the DVXα s.c.c. charge distributions gives a description of the metal–ligand bonding closely parallel to cellular ligand field (c.l.f.) treatments. Further comparison of DVXα s.c.c. and c.l.f. data indicates that the former gives not only a good account of '*d–s* mixing' in these systems but also quantitative confirmation of the empirical c.l.f. 'sum rule.' The present study suggests that the DVXα scheme provides independent validation of the underlying assumptions of the c.l.f. model in particular and ligand field theory in general.

Density functional methods,[1] of which the Xα or Hartree–Fock–Slater (HFS)[2] scheme is the simplest and best known, are remarkably successful at reproducing a wide variety of experimental properties.[3] Particularly in the field of transition-metal chemistry, this has been amply demonstrated by a number of recent applications.[4] It appears that, at least relative to *ab initio* Hartree-Fock (HF) theory, Xα calculations give accurate, reliable results even for very large molecules and clusters[5] but at a substantially reduced computational cost. In fact, Xα results are often in better agreement with experiment than the equivalent HF data.[3] The Xα approach is therefore becoming an increasingly important tool for the theoretical study of transition-metal systems.

A good test of any theoretical model is the prediction of electronic transition energies. Such calculations are often complicated by relaxation effects which lead to a breakdown of Koopmans theorem. At the HF level, ΔSCF calculations can account for relaxation but are time consuming. In contrast, the Xα transition-state method provides a fast convenient method for computing transition energies.

For Werner-type metal complexes, the absorption spectrum can be divided into two regions. The first comprises a set of relatively weak, low-energy bands associated with Laporte-forbidden *d–d* transitions. The second region is at higher energies with much more intense Laporte-allowed charge-transfer (c.t.) absorptions.

Ligand-field-theory (l.f.t) has traditionally provided the best treatment of *d–d* spectra. A particularly successful approach is the cellular ligand field (c.l.f.) model of Gerloch and Woolley.[6,7] Although such a scheme is necessarily empirical and parametric there is no doubt that the quantitative reproduction of *d–d* absorption energies for all d^n configurations is unequalled by any all-electron molecular orbital (m.o.) method. Of course, reproduction of experimental data alone is of limited value unless there exists a well defined connection between the ensuing ligand-field (l.f.) parameters and metal–ligand bonding. A thorough analysis[6] of the theoretical foundations of l.f.t. and its c.l.f. formulation has been given and a detailed picture of the nature of metal–ligand bonding can be extracted from the c.l.f. parameter values.[8]

Since only the *d*-orbitals are treated explicitly, l.f.t. cannot address directly the problem of c.t. spectra. On the other hand, all-electron models such as the Xα approach can, in principle at least, provide information on *d–d* and c.t. absorptions simultaneously. However, since a one-electron, single determinant scheme like the Xα model gives an incomplete treatment of many-electron multiplet states, a direct comparison between experimental and theoretical transition energies is only possible for d^1 and d^9 systems. Likewise, a spin-restricted formalism is a reasonable approximation only when there is one unpaired electron.

This paper examines the ability of the spin-restricted Xα model to reproduce the spectra of a series of d^9 chlorocuprate(II) complexes. These systems are attractive because they are chemically and electronically simple and yet display a sufficiently wide variety of co-ordination numbers and stereochemistries to provide a useful test. They have also been the subjects of numerous theoretical and experimental investigations.[9]

The particular computational scheme employed in this study is the numerical discrete variational Xα (DVXα) approach of Ellis and Painter.[10] The DVXα method takes advantage of the computational efficiency of Xα models but avoids the rather severe 'muffin-tin potential' approximation characteristic of the more familiar multiple scattering Xα (MSXα)[2] scheme.

Computational Details

The DVXα method is a numerical variant of the *ab initio* local density HFS[2] scheme. The details of the DVXα approach have been given many times[10,11] so that an outline of the procedure is all that is required here.

The DVXα model employs Slater's[12] exchange-correlation operator $V_{x\alpha}$ which for spin-up (↑) electrons is given by equation (1) where α is an adjustable parameter and $\rho\uparrow(1)$ is the charge

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* *Non-S.I. units employed:* eV ≈ 1.60×10^{-19} J, a.u. ≈ 5.29×10^{-11} m.

Table 1. Optimised s.c.c. valence-orbital populations derived from Mulliken analyses

Complex	Cu(3*d*)	Cu(4*s*)	Cu(4*p*)	Cl(3*s*)	Cl(3*p*)
$CuCl_4^{2-}$ (D_{4h})	9.428	0.495	0.452	1.973	5.683
$CuCl_4^{2-}$ (D_{2d})	9.402	0.435	0.515	1.974	5.688
$CuCl_5^{3-}$ (C_{4v})	9.394	0.411	0.413	1.976[a]	5.753[a]
				1.986[b]	5.878[b]
$CuCl_6^{4-}$ (D_{4h})[c]	9.388	0.403	0.349	1.981	5.830
$CuCl_6^{4-}$ (D_{4h})[d]	9.379	0.383	0.350	1.979	5.835

[a] Equatorial Cl populations. [b] Apical Cl populations. [c] $[Pt(NH_3)_4][CuCl_4]$. [d] $[NMeH_3]_2[CuCl_4]$.

$$V_{x\alpha\uparrow}(1) = -3\alpha[(3/4\pi)\rho\uparrow(1)]^{\frac{1}{3}} \qquad (1)$$

density for spin-up electrons. A similar expression holds for spin-down electrons. This simple dependence of the exchange on the charge density greatly facilitates the solution of the one-electron Schrödinger equation. A value for α of 0.7 has been found[11] to give good results for a variety of different chemical systems and has been used throughout the present work.

The various Coulomb and exchange integrals are approximated numerically by weighted summations over a three-dimensional grid of discrete sampling points.[10] The number of sample points, *N*, can be chosen to give the desired accuracy depending on the quantity of interest. Here, *N* varies between 3 200 and 3 800. This ensures that the Xα eigenvalues converge to within 0.002 eV of the limiting case of *N* approaching infinity. These points are distributed such that the central Cu atom has about 1 000 points associated with it. The remainder are equally divided amongst the Cl ligands.

Coulomb potentials are computed *via* the self-consistent charge (s.c.c.) procedure[13] which provides a good approximation to the molecular potential particularly for heteropolar interactions like the Cu–Cl bond. The potential is constructed from the gross atomic orbital populations obtained from a Mulliken population analysis. These populations also provide a convenient criterion for judging self consistency. The calculation is deemed converged when no population changes by more than a chosen amount (here 0.0005) from one iteration to the next.

As a numerical technique, the DVXα s.c.c. method is not restricted to analytical Gaussian or Slater basis sets. Any convenient radial functions may be used. A particularly compact set of approximately double-zeta quality may be generated from accurate solutions of the atomic Schrödinger equation within the Xα approximation.[14] However, only bound atomic functions have suitably contracted radial properties and there are only relatively few such orbitals for a given atom. To increase the variational freedom of the molecular calculation, the diffuse unbound functions can be localised by placing the atom in a potential well. Here, these so-called single site orbital (s.s.o.)[14] bases are computed relative to an applied 'funnel' potential of depth −2.0 a.u. at a radius of 4.0 a.u., decreasing linearly to zero at a radius of 6.0 a.u.

Most of the present work concerns spin-restricted calculations employing near-minimal atomic orbital basis sets: 1*s*–4*p* on copper and 1*s*–3*p* on chlorine. Of these, the copper 1*s*–3*p* and the chlorine 1*s*–2*p* core orbitals are 'frozen' and orthogonalised against the valence functions. Some extended-basis, spin-unrestricted computations for D_{2d} $CuCl_4^{2-}$ are described in the Discussion section. For the extended basis computations the true charge density is fitted to a multipole expansion centred on the atoms and comprising all multipoles with $l \leqslant 1$. There are six radial functions per centre.

The DVXα s.c.c. basis sets are optimised as described elsewhere.[4c] Essentially, a series of calculations are performed starting from Cu^{2+} $3d^9 4s^0 4p^0$ and Cl^- $3s^2 3p^6$ ionic basis sets. After each calculation, the new Mulliken populations are used to construct new bases and the molecular calculation is repeated. This 'double self-consistency' procedure is continued until the Mulliken populations differ by less than 0.02 with respect to the values used to generate the basis set. This process, although somewhat *ad hoc*, is simple and intuitively appealing. It also has the advantage of generating unique, different bases for each molecule. The optimised valence-orbital populations derived in this way are collected in Table 1.

Transition-state calculations[12] are also reported for *d–d* and c.t. absorptions. For a transition $\varphi_i \longrightarrow \varphi_0$ the energy is given by the orbital-energy difference from a calculation where the population of φ_i is decreased by 0.5 and that of φ_0 is increased by 0.5. All *d–d* transitions are calculated for both the optimised and ionic basis sets. C.t. energies are computed from the optimised basis set calculations only.

The relevant geometrical details of the five systems studied here are collected in Table 2. Structural data are from published *X*-ray diffraction studies although the stereochemistries have been slightly idealised to higher-symmetry point groups. The DVXα s.c.c. calculations refer to the complex ions found in the following compounds: $[NMe(CH_2CH_2Ph)H_2]_2(CuCl_4)$[15] ($D_{4h}$ $CuCl_4^{2-}$), $Cs_2[CuCl_4]$[16] (D_{2d} $CuCl_4^{2-}$), tris(*N*-benzylpiperazinium)pentachlorocuprate(II)[17] (C_{4v} $CuCl_5^{3-}$), and $[Pt(NH_3)_4][CuCl_4]$[18] (D_{4h} $CuCl_6^{4-}$). The bond lengths quoted for $[NMeH_3]_2[CuCl_4]$ (D_{4h} $CuCl_6^{4-}$) are estimated as the averages of the corresponding values in the ethylammonium[19] and ammonium[20] salts.

Results and Discussion

The results of the DVXα s.c.c. calculations for the chlorocuprate(II) complexes are presented in Tables 3 and 4. Both optimal and ionic basis-set data are given. Computed Xα orbital energies for D_{2d} $CuCl_4^{2-}$ are shown in Table 3. These data display features of the electronic structure representative of all the calculations, so that the following points apply equally well to the other systems.

First, the five highest-energy occupied orbitals have mainly metal 3*d* character. The singly occupied m.o. ($4b_2$) corresponds to the d_{xy} function in agreement with e.s.r. measurements.[9] That is, the DVXα model predicts the correct ground state. Below the mainly *d* levels is a set of mainly Cl 3*p* orbitals and below that the Cl 3*s* levels. The virtual orbitals correspond to the metal 4*s* and 4*p* functions.

Secondly, most of the valence levels have positive energies. This results[4c] from performing calculations on isolated, negatively charged complexes in the absence of the surrounding crystal. In the crystal, the potential arising from the neighbouring atoms stabilises the occupied levels.[21] However, calculations[21,22] which simulate the environment *via* a Madelung potential indicate that although the absolute orbital energies may change considerably, the relative energies remain largely unaffected.

Thirdly, as the basis set is optimised from the 'ionic' starting point, the 3*d* levels decrease in energy and spread out somewhat while the ligand-based orbitals rise in energy. At an atomic level, this appears to be counterintuitive. For a given (isolated) atom, the orbital energies increase as the number of electrons increases and *vice versa*.[12] Here, the copper atom gains electrons at the expense of the Cl ligands. The copper functions are expected to rise in energy as the chloride levels fall and indeed the basis-set calculations bear this out. For D_{2d} $CuCl_4^{2-}$, the copper 3*d*, 4*s*, and 4*p* orbitals rise from −29.28, − 21.09, and −13.87 to −12.86, −8.72, and −2.52 eV respectively (after correcting for the externally applied potential). Conversely, the Cl 3*s* and 3*p*

Table 2. Compound names, idealised geometries, geometrical data, and number of DV sample points for chlorocuprates(II). Bond lengths in Å, angles in °. See text for structural references

Compound	Complex	Symmetry	Cu–Cl$_{eq}$	Cu–Cl$_{ax}$	Cl$_{eq}$–Cu–Cl$_{eq}$	DV points
$[NMe(CH_2CH_2Ph)H_2][CuCl_4]$	$CuCl_4^{2-}$	D_{2d}	2.26		180.0	3 200
$Cs_2[CuCl_4]$	$CuCl_4^{2-}$	D_{2d}	2.23		129.2	3 199
a	$CuCl_5^{3-}$	C_{4v}	2.32	2.57	165.1	3 728
$[Pt(NH_3)_4][CuCl_4]$	$CuCl_6^{4-}$	D_{4h}	2.29	3.26	180.0	3 695
$[NMeH_3]_2[CuCl_4]$	$CuCl_6^{4-}$	D_{4h}	2.30[b]	2.90[b]	180.0	3 695

[a] Tris(*N*-benzylpiperazinium) pentachlorocuprate(II). [b] Average of values for ammonium and ethylammonium salts.

Table 3. DVXα s.c.c. orbital energies (eV) and main atomic orbital components for $CuCl_4^{2-}$ (D_{2d}) from ionic and optimised basis-set calculations

Orbital[a]	Ionic basis[b]	Optimised basis[b]	Main a.o. components[c]
$1a_1$	−9.6057	−8.5691	Cl(3*s*)
$1e$	−9.2818	−8.2629	Cl(3*s*)
$1b_2$	−9.1610	−8.1479	Cl(3*s*)
$2a_1$	0.3272	1.1904	Cl(3*p*) 88%, Cu(4*s*) 8%
$2e$	1.4343	2.1698	Cl(3*p*) 77%, Cu($3d_{xz,yz}$) 22%
$2b_2$	1.4937	2.0303	Cl(3*p*) 62%, Cu($3d_{xy}$) 38%
$1b_1$	1.7885	2.3804	Cl(3*p*) 72%, Cu($3d_{x^2-y^2}$) 28%
$3e$	2.1020	2.7529	Cl(3*p*) 85%, Cu($3d_{xy,yz}$) 14%
$3b_2$	2.1542	2.9110	Cl(3*p*)
$3a_1$	2.2787	2.8571	Cl(3*p*) 68%, Cu($3d_{z^2}$) 31%
$4e$	2.9055	3.7285	Cl(3*p*)
$1a_2$	3.0443	3.8799	Cl(3*p*)
$4a_1$	5.0194	4.4838	Cu($3d_{z^2}$) 66%, Cl(3*p*) 34%
$2b_1$	5.1852	4.6078	Cu($3d_{x^2-y^2}$) 68%, Cl(3*p*) 32%
$5e$	5.3897	4.9488	Cu($3d_{xz,yz}$) 60%, Cl(3*p*) 40%
$4b_2$ (h.o.m.o.)	5.9374	5.6153	Cu($3d_{xy}$) 54%, Cl(3*p*) 46%
$5a_1$ *	12.2771	12.6135	Cu(4*s*)
$5b_2$ *	14.2634	14.2276	Cu($4p_z$)
$6e$ *	16.9728	17.0033	Cu($4p_{x,y}$)

[a] Virtual orbitals are marked with an asterisk (*). [b] Energies in eV. [c] Percentage composition of m.o.s derived from Mulliken population analysis of optimised basis set results. Where explicit percentage not given, that orbital contributes >95%.

levels fall from −8.26 and 3.06 to −11.75 and −0.26 eV respectively. In a molecule, however, the influence of the neighbouring atoms must be considered.

Great care must be exercised when trying to compare m.o. energies for the molecule with those of the (notional) constituent parts. This has recently been shown[23] in detail for the simplest case of H_2. Relative to the isolated atoms, there is the potential arising from the surrounding bonded atoms. This includes additional one-electron (Coulomb) and two-electron (exchange) components. In D_{2d} $CuCl_4^{2-}$, for example, each ligand is bound only to the central metal while the Cu atom has four Cl neighbours. The interelectron repulsion arising from bond formation is therefore more pronounced for copper than for chlorine. In the molecule, this is sufficient to raise the valence metal orbitals above the valence chlorine functions even though the 3*d* orbital energy of the isolated copper atom of the basis-set calculation is many eV lower than the chloride 3*p* energy.

Of course, the more usual m.o. calculation would probably use fixed basis sets appropriate to neutral Cu and Cl atoms in which case the Cu 3*d* orbitals are higher in energy than the Cl 3*p* functions. This is not the case for the optimised basis sets used here and the relative changes in m.o. energies as the basis is optimised still require explanation.

Returning to those m.o. energy changes, the lowering of the mainly 3*d* levels correlates with the decreasing chloride potential as a result of the decreasing ligand charge. Conversely, the metal potential is increasing leading to an increase in the mainly Cl 3*p* levels. Both trends are in the opposite sense to the basis atomic orbital energy changes. The concomitant enhancement of the M–L covalency accounts for the larger splitting of the mainly *d* levels of the optimised basis calculation.

Table 4. '*d–d*' Orbital-energy differences (cm^{-1}) for chlorocuprate complexes

Complex	Transition	Ionic basis	Optimised basis	Experiment[a]
$CuCl_4^{2-}$ (D_{2d})	$5e \longrightarrow 4b_2$	4 417	5 375	4 800, 5 550
	$2b_1 \longrightarrow 4b_2$	6 067	8 125	7 900
	$4a_1 \longrightarrow 4b_2$	7 404	9 126	9 050
$CuCl_4^{2-}$ (D_{4h})	$2b_{2g} \longrightarrow 3b_{1g}$	10 044	13 340	12 500
	$2e_g \longrightarrow 3b_{1g}$	11 413	14 032	14 300
	$3a_{1g} \longrightarrow 3b_{1g}$	13 542	17 774	17 000
$CuCl_5^{3-}$ (C_{4v})	$6a_1 \longrightarrow 4b_1$	6 655	6 260	≈6 700
	$6e \longrightarrow 4b_1$	8 617	10 225	11 050
	$2b_2 \longrightarrow 4b_1$	8 249	11 129	11 050
$CuCl_6^{4-}$ (D_{4h}) $[Pt(NH_3)_4]^{2+}$	$2b_{2g} \longrightarrow 3b_{1g}$	8 887	11 730	10 900[b]
		(8 713)	(11 635)	
	$3e_g \longrightarrow 3b_{1g}$	9 532	12 056	13 100[b]
		(9 266)	11 855	
	$5a_{1g} \longrightarrow 3b_{1g}$	10 061	12 525	14 300[b]
		(8 996)	(11 545)	
$CuCl_6^{4-}$ (D_{4h}) $[NMeH_3]^+$	$5a_{1g} \longrightarrow 3b_{1g}$	7 500	9 286	10 800[b]
		(6 401)	(7 004)	
	$2b_{2g} \longrightarrow 3b_{1g}$	8 469	11 292	12 220[b]
		(8 288)	(11 161)	
	$3e_g \longrightarrow 3b_{1g}$	8 909	11 607	13 300[b]
		(8 646)	(11 314)	

[a] Experimental data (in order): J. Ferguson, *J. Chem. Phys.*, 1964, **40**, 3406; ref. 32*b*; ref. 17; W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, 1964, **3**, 841; C. Furlani, A. Scamellotti, F. Magrini, and D. Cordischi, *J. Mol. Spectrosc.*, 1967, **24**, 270. [b] Assignments per ref. 29.

Comparison with d–d *Spectra.*—The calculated orbital-energy differences and experimental *d–d* band maxima are presented in Table 4. The data in column 1 relate to ionic basis calculations while those in column 2 are optimised basis results. With the exception of the lowest-energy band for $CuCl_5^{3-}$, the ionic basis-set energies are around 20—30% lower than observed. In contrast, the optimised basis-set energies are in remarkably good agreement with the experimental band maxima. The calculated values are within 7% of experiment for both $CuCl_4^{2-}$ species and for $CuCl_5^{3-}$, within 10% for the platinum $CuCl_6^{4-}$ complex, and within 12% for the $[NMeH_3]^+$ $CuCl_6^4$ species. The larger discrepancy for the latter may be partly due to a small error in the assumed bond lengths.

The DVXα model gives an excellent account of the *d–d* spectra in chlorocuprates(II), apparently without the need for transition-state calculations (see below). However, theory does seem to underestimate the d_{xz}, d_{yz} − d_{xy} π-type splitting in the

Table 5. Comparison of calculated orbital-energy differences (cm^{-1}) from various methods with the present DVXα and experimental results

$CuCl_4^{2-}$ (D_{2d})	$^2B_2 \rightarrow {}^2E$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$
Extended Hückel[a]	8 641	11 521	12 962
INDO[b]	4 622	6 535	6 852
MSXα (tangent spheres)[b]	5 500	11 380	10 850
MSXα (overlapping spheres)[c]	5 575	8 946	9 709
DVXα[d]	5 375	8 125	9 126
Experiment[e]	4 800, 5 550	7 900	9 050

$CuCl_4^{2-}$ (D_{4h})	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$	$^2B_{1g} \rightarrow {}^2A_{1g}$
Wolfsberg-Helmholtz[f]	5 856	6 887	9 278
RHF[g]	7 500	9 400	10 100
UFH[b]	7 300	8 500	9 500
INDO[b]	12 950	14 050	13 080
MSXα (overlapping spheres)[c]	14 407	14 788	17 035
DVXα[d]	13 340	14 032	17 774
Experiment[h]	12 500	14 300	17 000

$CuCl_6^{4-}$ [$NMeH_3$]	$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$
INDO[b]	6 600	8 811	9 362
Extended Hückel[i]	9 436	20 404	21 130
DVXα[d]	9 286	11 292	11 607
Experiment[j]	10 800	12 200	13 300

[a] Interpolated from Figure 2 (in L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, 1963, **2**, 911) at a bond length of 2.30 Å. [b] Ref. 24. [c] Ref. 25. [d] This work. [e] J. Ferguson, *J. Chem. Phys.*, 1964, **40**, 3406. [f] P. Ros and G. C. A. Schuit, *Theor. Chim. Acta*, 1966, **4**,1; J. Demuynk, A. Veillard, and U. Wahlgren, *J. Am. Chem. Soc.*, 1973, **95**, 5563. [h] Ref. 32*b*. [i] L. L. Lohr, *Inorg. Chem.*, 1967, **6**, 1890. Bond lengths used were Cu–Cl$_{eq}$ 2.325 and Cu–Cl$_{ax}$ 2.55 Å. [j] C. Furlani, A. Scamellotti, F. Magrini, and D. Cordischi, *J. Mol. Spectrosc.*, 1967, **24**, 270.

tetragonal systems by a factor of between 3 and 7. This result stems from an underestimation of Cl π bonding parallel to the equatorial plane, as described later in connection with the charge-density analysis.

Note that there are two entries in Table 4 for each of the $CuCl_6^{4-}$ species. These data illustrate not only an interesting feature of the chemistry of these two complexes but also the sensitivity of the DVXα s.c.c. scheme.

The figures in parentheses were obtained by assigning different basis sets and potential types to axial and equatorial Cl ligands. This seems natural since the calculations are performed on isolated $CuCl_6^{4-}$ species and it is certainly true that the axial and equatorial ligands are different by symmetry. However, the agreement with experiment is significantly poorer particularly for the $5a_{1g} \longrightarrow 3b_{1g}$ (*i.e.* $d_{z^2} \longrightarrow d_{x^2-y^2}$) transition of the methylammonium complex. This transition is sensitive to the nature of the axial ligand. The crystal structures of both complexes[18,19] show that the axial ligand of one $CuCl_6^{4-}$ complex is the equatorial ligand of an adjacent $CuCl_6^{4-}$ species. Hence, axial and equatorial Cl ligands should have the same potential: they are different by symmetry but essentially the same by chemistry. The Xα calculations were thus repeated using common basis sets and potential types for all six ligands. Agreement with experiment is certainly better. Not only are the energies improved but the calculated assignments are consistent with c.l.f. predictions. The implications for l.f.t. are discussed further below.

Previous M.O. Studies.—A comparison with published m.o. calculations reveal that the DVXα s.c.c. method gives better *d–d* transition energies than HF or MSXα approaches. Correo de Mello *et al.*[24] have performed a detailed comparison of *ab initio* HF, MSXα (tangent spheres), and incomplete neglect of differential overlap (INDO) results for planar $CuCl_4^{2-}$. They conclude[24] that MSXα and INDO transition energies are numerically comparable to the observed band maxima but the calculated assignments disagree with experiment. On the other hand, *ab initio* HF theory (either spin-restricted RHF or spin-unrestricted UHF) gives the correct assignment but absolute values about 40% lower than observed.

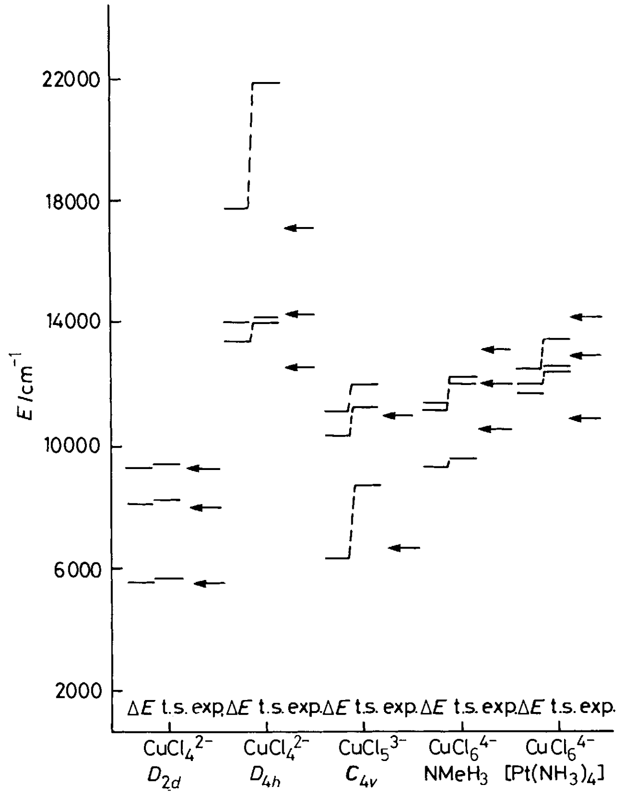

Figure 1. Orbital-energy differences, ΔE (long bars, left) transition-state energy diferences, t.s. (long bars, right), and experimental band energies (arrows) for the *d–d* spectra of chlorocuprates. All values in cm^{-1}

Table 5 illustrates this point by comparing calculated orbital-energy differences from the methods mentioned above as well as with some extended Hückel and overlapping-spheres MSXα data. The DVXα s.c.c. method gives the best agreement with experiment followed by the overlapping-spheres MSXα approach. The latter might be expected to produce quite similar results to the DVXα s.c.c. model since both schemes describe the molecular potential as a set of overlapping spheres.[13] However, the DVXα s.c.c. method has the advantage of determining the extent of overlap self-consistently and does not become inconsistent as the degree of 'sphere overlap' increases.[25]

Transition-state Calculations.—So far, the discussion has concentrated on the agreement between *d–d* spectra and theoretical orbital-energy differences. Within the Xα approximation, Slater's transition-state formalism[12] is supposedly a better method for computing ionisation potentials and transition energies.

Table 6 collects the calculated transition-state energies for planar and distorted tetrahedral $CuCl_4^{2-}$ from two MSXα studies[24,25] and the present DVXα results for ionic and optimised basis sets while Figure 1 compares the DVXα ground-state orbital-energy differences and transition-state values from optimised basis-set calculations with experiment. For D_{2d} $CuCl_4^{2-}$ there is very little change while for D_{4h} $CuCl_4^{2-}$ the agreement has worsened. (Similar results emerged from an

Table 6. Xα transtion-state calculations for *d–d* transitions of $CuCl_4^{2-}$ (D_{2d} and D_{4h}). All values in cm^{-1}

$CuCl_4^{2-}$ (D_{2d})	$^2B_2 \rightarrow {}^2E$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$
MSXα[a]	5 636	9 348	9 962
MSXα[b]	4 263	6 599	7 158
DVXα (Ionic basis)[c]	4 545	6 478	7 813
DVXα (Optimised basis)[c]	5 399	8 396	9 203
Experiment	4 800, 5 550	7 900	9 050
$CuCl_4^{2-}$ (D_{4h})	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$	$^2B_{1g} \rightarrow {}^2A_{1g}$
MSXα[a]	15 286	15 065	19 502
MSXα[b]	12 308	12 247	16 038
DVXα (Ionic basis)[c]	10 865	12 037	15 263
DVXα (Optimised basis)[c]	14 077	14 168	21 876
Experiment	12 500	14 300	17 000

[a] Ref. 25. [b] A. A. Gewirth and E. I. Solomon, *J. Am. Chem. Soc.*, 1988, **110**, 3811. [c] This work.

overlapping-spheres MSXα study[25] *cf.* data in Table 5 and Table 6. For $CuCl_5^{3-}$, the lower-energy band increases by some 2 500 cm^{-1} to lie about 2 000 cm^{-1} above the observed[17] absorption maximum but the higher-energy transitions appear to approach experiment more closely. Numerical agreement for the two $CuCl_6^{4-}$ species is marginally better but the ordering of the d_{xy} and d_{xz}, d_{yz} levels is inverted relative to that observed. Overall, the transition-state calculations for the *d–d* bands have a relatively small effect, except perhaps for planar $CuCl_4^{2-}$, but if anything the agreement with experiment worsens.

This result suggests that DVXα optimised-basis-set orbital-energy differences are sufficient for predicting the *d–d* spectra of these systems. Yet, this need not imply a 'failure' of the Xα method or the transition-state formalism. Indeed, from a l.f. viewpoint, such a conclusion is to be expected *a priori.*

In a single determinant approach such as HF theory, the difference between two eigenvalue (or m.o.) energies equals the difference in total energies of the two molecular states involved in the transition.[12,26] This is the essence of Koopmans theorem[27] but it applies rigorously only if there is no orbital relaxation accompanying the transition. In contrast, the Xα eigenvalue for oribital φ_i is a partial derivative of the total energy $\langle E\rangle$ with respect to the orbital's occupation number q_i as in equation (2). The total energy difference $\Delta E_{x\alpha}$, which is the

$$e_{x\alpha}(\varphi_i) = \delta\langle E\rangle/\delta q_i \qquad (2)$$

transition energy, is not given simply as an eigenvalue difference as in HF theory. Instead, there are additional second-, third-, and higher-order corrections [equation (3)]. Slater[12] has

$$\begin{aligned}\Delta E_{x\alpha} = {} & e_{x\alpha}(\varphi_i) - e_{x\alpha}(\varphi_j) + \\ & (1/2!)(-\delta^2\langle E\rangle/\delta q_i^2 + 2\delta^2\langle E\rangle/\delta q_i\delta q_j - \delta^2\langle E\rangle/\delta q_j^2) + \\ & (1/3!)(\delta^3\langle E\rangle/\delta q_i^3 - 3\delta^3\langle E\rangle/\delta q_i^2\delta q_j + 3\delta^3\langle E\rangle/\delta q_i\delta q_j^2 - \\ & \delta^3\langle E\rangle/\delta q_j^3) + \ldots \qquad (3)\end{aligned}$$

shown, however, that for a hypothetical transition state, in which the appropriate orbitals have occupations halfway between the initial and final states, the leading second-order correction term vanishes and the third-order term is reduced by a factor of four.

The present DVXα s.c.c. results are in good agreement with experimental *d–d* spectra without the need for transition-state calculations. The second-order terms appear to be of minor importance. These terms describe the rate of change of the total energy as a function of the orbital occupations[12] and are either small or roughly constant for all the relevant orbitals. Here, the relevant functions are the mainly *d* orbitals and the implication is that the rearrangements of the *d* electrons occurring for the *d–d* transitions has little effect on the total molecular energy. In short, the *d* orbitals appear to be 'uncoupled' from the rest of the molecular charge. This suggestion has for many years been cited[6] as the principal reason for the success of l.f.t.

Implications for Ligand-field Theory.—Ligand-field models have been employed for over 50 years to rationalise the spectra and magnetism of transition-metal complexes. One of the main aims of these studies is to comment on the nature of metal–ligand bonding. It is only relatively recently that the full potential of l.f.t. as a probe of the M–L bond has been realised.

The cornerstone of this development is the theoretical analysis of Gerloch and Woolley[6] particularly with respect to the c.l.f. model. The c.l.f. scheme describes the essentially local M–L bonding *via* parameters which reflect the local σ and π symmetry. Guided by the underlying l.f. formalism, a transparent chemical interpretation of the resulting c.l.f. parameter values emerges.[7,8]

A number of recent applications[28] demonstrate the utility of the c.l.f. approach. Of interest here are two ligand-field analyses of chlorocuprate(II) complexes. One[29] deals with tetragonal complexes while the other[30] investigates the D_{2d} $CuCl_4^{2-}$ ion in detail. The former study is discussed first.

Tetragonal chlorocuprates display a varied axial co-ordination ranging from about 2.78 Å for $CuCl_6^{4-}$ in $CsCuCl_3$[31] to essentially nothing for truly square-planar $CuCl_4^{2-}$ species.[15] The spectrum of planar $CuCl_4^{2-}$ has been thoroughly studied by Hitchman and co-workers[32] and the assignment of the *d–d* bands seems to be settled. In particular, the highest-energy band at around 17 000 cm^{-1} is assigned to the transition from d_{z^2} (*i.e.* $^2B_{1g} \longrightarrow {}^2A_{1g}$).

Early crystal field (c.f.) and angular overlap model (a.o.m.) treatments calculated this transition about 6 000 cm^{-1} lower than observed. Smith[33] accounted for this apparent anomaly by expanding the a.o.m. to include explicit *d–s* mixing. In D_{4h} symmetry, the $3d_{z^2}$ and 4*s* orbitals both transform as a_{1g} and may mix. The resulting configuration interaction depresses the d_{z^2} energy leading to a higher predicted transition energy.

Within the c.l.f. framework, there is no anomaly and no artificial extension of the formalism is necessary.[34] The space around the metal is divided into spatially discrete regions or cells. Each cell is normally associated with an individual bond such that the potential in a cell can be associated exclusively with the bonding interaction it contains.[6] However, to maintain consistency for a planar complex, the cells above and below the molecular plane must still be parameterised explicitly. These 'co-ordination voids,' despite the lack of a discrete ligand, still contain electron density which exerts a pronounced l.f. effect.

The void cells in planar $CuCl_4^{2-}$ are characterised by c.l.f. e_σ values of around -3 000 cm^{-1}.[34] The negative values lead to the required depression of the d_{z^2} energy. However, although apparently unusual, a negative e_σ value is completely consistent with the c.l.f. formalism.[6,34] The void cell contains valence metal *s*-electron density. The metal *s* function is at higher energy than the basis *d* orbitals and hence the interaction leads to a net stabilisation of d_{z^2}. This is the c.l.f. equivalent of *d–s* mixing.

As the strength of the axial ligation increases, the co-ordination void is gradually pre-empted by the bonding electron density. The e_σ values are expected to change smoothly from moderately large and negative to large and positive. This process has been mapped out empirically[34] for a series of tetragonal copper(II) amine complexes.

The DVXα s.c.c. model 'automatically' includes *d–s* mixing. For D_{4h} $CuCl_4^{2-}$, the energy of the d_{z^2} orbital relative to the highest occupied molecular orbital (h.o.m.o.) ($d_{x^2-y^2}$) is in excellent agreement with experiment (see Table 4). However, there is an important distinction between the c.l.f. and a.o.m./DVXα s.c.c. treatments. In the former, there is an explicit

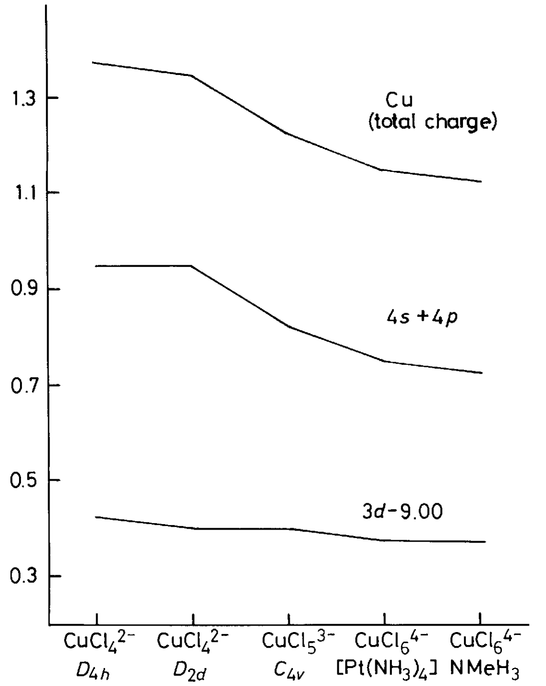

Figure 2. Variation of orbital populations for chlorocuprates. Values computed from Mulliken population analyses of optimised basis-set calculations

separation between the d electrons and the 'rest.' That is, in l.f.t. the bonding functions which perturb the d orbitals have not only a ligand component but also include the valence metal s and p orbitals.[6] The main bonding interaction results from a mixing of ligand orbitals with these valence metal s and p functions. The d orbitals either play a relatively minor role or are all involved to about the same extent.

Returning to the c.l.f. analyses of tetragonal chlorocuprates, several possible sets of c.l.f. parameter values emerge[29] since many of the systems lack definitive spectral assignments. A choice between these sets was made on the basis of the 'sum rule'.[29,35] Within the c.l.f. model, the sum, Σ, of all the (locally diagonal) parameter values [equation (4) where N is the

$$\sum = \sum_i e_\lambda, \lambda = \sigma, \pi_x, \pi_y; i = 1,2,\ldots, N \qquad (4)$$

number of cells] is proportional to the spherically symmetric part of the l.f. potential. As described by Woolley,[36] this is equivalent to Σ equalling the trace of the l.f. matrix. For a series of related complexes, Σ is expected to remain fairly constant reflecting Pauling's electroneutrality principle. Indeed, a value of $21\,000 \pm 600$ cm^{-1} emerges for a series of copper(II) amine species.[34] The assumption of a 'sum rule' for chlorocuprate complexes suggests a Σ value of around 23 000 cm^{-1}.[29]

Using this value for Σ leads to quite different assignments for the two $CuCl_6^{4-}$ complexes treated in this work. In particular, the $^2B_{1g} \longrightarrow {}^2A_{1g}$ transition is the lowest band for the $[NMeH_3]^+$ complex while it is the highest-energy absorption for the platinum complex. The DVXα s.c.c. assignments agree but only after due recognition is made of the environment of the $CuCl_6^{4-}$ ions. The two methods give the same result by completely different routes. The DVXα calculations appear to provide independent confirmation of the validity of the c.l.f. 'sum rule.'

The detailed nature of the 'sum rule' is not yet fully understood[35] but it seems to be related to the notion of a constant amount of charge donation from metal to ligand. Within the c.l.f. framework the implication is that the spherical part of the l.f. potential must be fairly constant. Since this part defines the (notional) d-orbital basis, a constant Σ presumably means that the d-orbital bases are the same. That is, they have the same radial wavefunction. Confirmation of this proposition may be found in the DVXα s.c.c. calculations.

Figure 2 shows the variation of the optimal-basis d-orbital populations from the 'initial' d^9 configuration, the sum of the 4s and 4p populations, and the sum of both of these. The latter two show a fairly marked change with respect to co-ordination number, decreasing by about 0.25 electrons. In contrast, the d populations remain essentially the same. Hence the DVXα radial functions for the d orbitals, optimised for each molecule. remain constant and the c.l.f. and DVXα methods are in accord once more.

Figure 2 also shows that the net charge on the metal varies quite considerably across the series of complexes (from +0.6 to +0.9). The naive interpretation of the 'sum rule' reflecting a constancy in this total charge is seen to be invalid. Such a view implicitly divides the electron density into a metal part and a ligand part. This is inappropriate in a l.f. context where the correct partition is into d-electron density and 'the rest.'

Outside of l.f.t., however, net atomic charges may still have significance. For example, an X-ray analysis[16] of the crystal forces and charge distributions in $Cs_2[CuCl_4]$ predicts net charges of 0.60 and −0.65 for Cu and Cl atoms in D_{2d} $CuCl_4^{2-}$. The present DVXα s.c.c. calculations compare very favourably giving values of 0.65 and −0.66 respectively. The good treatment of net atomic charges by the DVXα s.c.c. method has been noted[4c] in other contexts also.

If the c.l.f. 'sum rule' monitors the spherical potential around the d orbitals, then the individual c.l.f. parameters describe the locally aspherical features in the potential. The source of this potential has been identified[6] as the bonding electron density. In order to make the correct connection between DVXα s.c.c. charger densities and c.l.f. parameter values, it is important to remember that l.f.t. explicitly separates the d electrons from the rest. The bonding functions, which are spatially and energetically closest to the d orbitals and exert the largest influence, comprise both ligand and metal components. However, within the DVXα s.c.c. framework the Mulliken population analysis ensures that the largest perturbation to the d orbitals will come from the metal part of the bonding orbitals since the ligand functions are too far away. Therefore, the 4s and 4p populations should correlate with the c.l.f. parameters.

Table 7 presents a breakdown of the calculated 4s and 4p populations into local σ and π components and compares these values with the c.l.f. e_σ and e_π values. The qualitative correspondence is very good. The trends displayed in the DVXα charges are reproduced by the e_λ values except for the e_π(equatorial) value in the platinum $CuCl_6^{4-}$ complex which appears too large. This is probably due to the experimental uncertainties of the c.l.f. analysis.[29] In general, the agreement would have been even better if the DVXα s.c.c. calculations predicted greater π donation in the equatorial plane. The Cl ligands do not behave as 'linear ligators' in the DVXα scheme. The in-plane donation is underestimated by a factor of 8—10 which accounts for the computed $d_{xy} - d_{xz}, d_{yz}$ splittings being rather less than observed.

The changes in the d_{z^2} populations, $\Delta\rho(d_{z^2})$, given in Table 7 measure the extent of d–s mixing. For the tetragonal complexes the $\Delta\rho(d_{z^2})$ values correlate very well with the e_σ(void) data also.

To summarise, the calculated charge distribution and the c.l.f. parameters values appear to give very similar accounts of the M–L bonding in these chlorocuprates. It is gratifying to obtain the same chemistry whether from a method which computes the charge density or from a method which analyses spectroscopic transitions. In contrast, X-ray diffraction studies[37] apparently give very different results from l.f. treatments. It is claimed[37]

Table 7. Comparison of DVXα charge densities with c.l.f. e_λ parameter values (from refs. 29 and 30). See text for explanation of derivation of DVXα charge densities

	$CuCl_4^{2-}$ (D_{2h})		$CuCl_6^{4-}$ (Pt)[a]		$CuCl_6^{4-}$ (Me)[b]		$CuCl_4^{2-}$ (D_{2d})	
	DVX_α	c.l.f	DVX_α	c.l.f.	DVX_α	c.l.f.	DVX_α	c.l.f.
σ_{eq}	0.1627	5 300	0.1552	5 100	0.1409	4 800	0.1577	5 000—4 500
π_{eq}	0.0319	850	0.0190	1 100	0.0139	550	0.0375	≈750—875
σ_{eq}/π_{eq}	5.1	6.2	8.2	4.6	10.1	8.7	4.2	6.7—5.1
σ_{ax}		−3 200	0.0264	−2 050	0.0438	−600		−400 to −900
π_{ax}			0.0007		0.0017			
$\Delta\rho(d_{z^2})$[c]	0.0434		0.0254		0.0164		0.0088	

[a] $[Pt(NH_3)_4][CuCl_4]$. [b] $[NMeH_3]_2[CuCl_4]$. [c] $\Delta\rho(d_{z^2}) = 2.0 - \rho(3d_{z^2})$ where $\rho(3d_{z^2})$ is the Mulliken population.

that the two approaches actually measure different things but given the technical and mathematical problems associated with deriving accurate and/or unique valence-orbital populations from a least-squares treatment of *X*-ray data, this conclusion appears suspect. The present results suggest both methods should lead to the same description of the bonding.

An Analysis of D_{2d} $CuCl_4^{2-}$ *and* $CuCl_5^{3-}$.—The best agreement between calculated and observed *d–d* transition energies is for the D_{2d} $CuCl_4^{2-}$ complex. Prompted by the 'sum rule' results for the tetragonal chlorocuprates,[28] this system has also been reanalysed within the c.l.f. framwork,[30] Since both approaches quantitatively reproduce experiment, they may be expected to predict very similar chemistries.

The c.l.f. analysis[30] suggested that the assumption of linear ligation should be relaxed for D_{2d} $CuCl_4^{2-}$. The π parameter parallel to the S_4 axis ($e_{\pi\parallel}$) should be larger than in the perpendicular direction. A breakdown of the DVXα s.c.c. 4*s* and 4*p* populations gives $\rho(\pi_\parallel) = 0.0408$ and $\rho(\pi_\perp) = 0.0341$ in agreement with this proposition. The c.l.f. study further indicated a small void cell contribution associated with the larger Cl–Cu–Cl angle of 129.2°. The value of e_σ(void) = −850 cm^{-1} appears to be too negative given that $\Delta\rho(d_{z^2})$ for $CuCl_4^{2-}$ (0.0088) is less than that for the $[NMeH_3]^+CuCl_6^{4-}$ complex where e_σ(void) = −600 cm^{-1} (see Table 7). Nevertheless, even at a very detailed level, the c.l.f. and DVXα s.c.c. models concur quite well.

If the conclusions emerging from this analysis of simple chlorocuprate complexes prove to be more general, a combined l.f./DVXα approach may prove to be a very powerful tool indeed. For example, ambiguous spectral assignments may be resolved by DVXα calculations leading to unique c.l.f. parameter values. Alternatively, a DVXα calculation may fill in some gaps in a sparse experimental spectrum. The latter is less satisfactory since the Xα transition energies may still be in error by 1 000 cm^{-1} or more. This point is illustrated by analysing $CuCl_5^{3-}$.

Four c.l.f. parameters are required—e_σ(eq), e_π(eq), e_σ(ap), and e_π(ap), where eq and ap refer to equatorial and apical chlorides respectively. There are only two *d–d* bands reported[17] at 6 700 and 11 050 cm^{-1}. In conjunction with the sum rule ($\Sigma = 23\,000$), there remains one degree of indeterminacy. The DVXα s.c.c. calculation predicts a third band at 10 200 cm^{-1} (Table 3). Using the experimental geometry[17] and the expressions of Hitchman[38] gives e_σ(eq) = 4 211, e_π(eq) = 299, e_σ(ap) = 1 675, and e_π(ap) = 1 035 cm^{-1}. While the equatorial parameters appear reasonable, e_π(ap) is certainly too large. Moreover, the longer Cu–Cl(ap) bond length of 2.57 Å[17] coupled with the co-ordination void opposite suggests e_σ(ap) is also too large {*cf.* $[Cu(NH_3)_4L]$, L = NH_3, e_σ(L) = −750 cm^{-1}; L = H_2O, e_σ(L) = −4 500 cm^{-1}}.[34]

Charge-transfer Transitions.—Table 8 compares calculated and observed c.t. transition energies for three complexes. The first two columns relate to orbital-energy differences from the ionic basis-set calculations with the next two derived from transition-state calculations based on the optimised basis results. The last two columns present experimental data with assignments taken from Solomon and co-workers.[39] For these bands, energy differences, Δ*E*, relative to the lowest-energy c.t. band are also given in parentheses.

It is remarkable how well the ionic-basis orbital-energy differences agree with observation. However, in the absence of further data, this result may well be fortuitous. First, the ionic-basis calculations do not reproduce the *d–d* spectra very accurately either as orbital-energy differences or *via* transition-state calculations (Table 6). Secondly, while such transition-state calculations are apparently unnecessary for *d–d* bands, it is difficult to see how a similar result could obtain for c.t. absorptions. The movement of charge from metal to ligand perturbs the molecular potential significantly and the second-order terms in equation (3) are more important. The agreement obtained here may well be accidental.

For the optimised basis-set results, transition-state calculations increase the predicted c.t. energies by 10 000—20 000 cm^{-1} to give values 4 000—10 000 cm^{-1} larger than observed. However, the Δ*E* values accord quite well indicating that the splitting of the mainly ligand orbitals is in agreement with experiment. Solomon's overlapping-spheres MSXα study[39] gave a similar result except the calculated c.t. bands were about 7 000 cm^{-1} too low. The difference between the DVXα s.c.c. and the MSXα results can be traced to the choice of single site orbital (s.s.o) basis sets.

A series of extended basis-set calculations were performed for D_{2d} $CuCl_4^{2-}$. The s.c.c. approximation was replaced by the more accurate method of fitting the potential *via* a multipole expansion. All terms with $l \leqslant 1$ were included. Various combinations of 4*d*, 5*s*, and 5*p* functions on Cu and 3*d*, 4*s*, and 4*p* orbitals on Cl were investigated. The results are displayed in Table 9. It is apparent that the inclusion of a Cu 4*d* set into the near-minimal basis is sufficient to recover the results of Solomon. In no case did the mainly *d*-orbital energies vary by more than 800 cm^{-1} which suggests that the s.c.c. approximation, the near-minimal s.s.o. bases, and the spin-restricted formalism are all relatively unimportant, at least for chlorocuprates.

Neither the DVXα s.c.c. nor MSXα method appears capable of predicting the barycentre of the Cl 3*p* levels. As noted previously,[24] this is probably due to the 3*p* level being unbound within the Xα approximation at least for values of α around 0.7. Other ligands such as H_2O or NH_3 do not suffer from this problem and it will be interesting to examine how well the DVXα s.c.c. scheme can predict c.t. states for aqua or amine complexes.

Nevertheless, the present results for chlorocuprates are very encouraging. Future studies are aimed at extending this work to more complex systems and other metals with different d^n

Table 8. Calculated and observed c.t. transitions. The ionic basis-set results are orbital-energy differences while the optimised basis-set data are from transition-state calculations for experimentally assigned bands. ΔE values in parentheses are with respect to the $1a_2$ levels

Complex	m.o.	ΔE (Orbital) Ionic basis		ΔE (Transition state) Optimised basis		Experiment	
$CuCl_4^{2-}$ $(D_{2d})^a$	$1a_2$	23 333	(0)	27 090	(0)	22 700	(0)
	$4e$	24 452	(1 119)	27 965	(875)	24 730	(2 050)
	$3a_1$	29 507					
	$3b_2$	30 512					
	$3e$	30 933	(7 600)	31 295	(4 205)	28 880	(6 180)
	$1b_1$	33 461					
	$2b_2$	35 838					
	$2e$	36 318	(12 985)	37 318	(10 228)	33 480	(10 780)
	$2a_1$	45 246	(21 913)	46 197	(19 107)	43 000	(20 300)
$CuCl_5^{3-}$ $(C_{4v})^b$	$1a_2$	23 839	(0)	29 732	(0)	23 260	(0)
	$5e$	21 742	(−	32 916	(3 184)	27 030	(3 770)
	$5a_1$	27 927	2 097)	35 088			
	$4e$	28 252		34 896	(5 164)	27 030	(3 770)
	$3b_1$	29 287	(4 413)	35 001			
	$3e$	33 537		37 363			
	$4a_1$	35 955		41 210			
	$2b_1$	37 928		34 695			
	$1b_2$	39 019		42 641			
	$2e$	40 344		44 400	(14 668)	37 740	(14 480)
	$3a_1$	49 330	(16 505)	51 627			
$CuCl_6^{4-}$ $(NMeH_3)^a$	$1a_{2g}$	25 881		34 093	(0)	23 700	(0)
	$4e_u$	30 245	(0)	37 914	(3 821)	26 400	(3 650)
	$3a_{2u}$	30 249	(4 364)				
	$2e_g$	30 352					
	$1b_{2u}$	30 826					
	$3e_u$	33 301		43 473	(9 380)	33 300[c]	(9 300)
	$4a_{1g}$	35 705	(7 420)				
	$1e_g$	37 480					
	$2b_{1g}$	40 079					
	$2a_{2u}$	40 648					
	$1b_{2g}$	40 921					
	$2e_u$	42 332		49 151	(15 058)	37 400	(13 700)
	$3a_{1g}$	51 807	(16 451)	56 545	(22 452)	49 000[c]	(25 000)
			(25 926)				

[a] Experimental bands from ref. 39. [b] Experimental bands from ref. 17. [c] R. D. Willett, O. L. Liles, and C. Michelson. *Inorg. Chem.*, 1967, **6**, 1885.

Table 9. Transition-state calculations of the lowest c.t. band for D_{2d} $CuCl_4^{2-}$ for various s.s.o. basis sets

Method	DVXα basis	$\Delta E(1a_2 \longrightarrow 4b_2)$
s.c.c. spin restricted	Cu 1*s*–4*p*; Cl 1*s*–3*p*	27 090
s.c.c. spin unrestricted	Cu 1*s*–4*p*; Cl 1*s*–3*p*	28 708
DVM * spin unrestricted	Cu 1*s*–4*p* + 5*s*, 5*p*; Cl 1*s*–3*p* + 4*s*, 4*p*	28 782
	Cu 1*s*–4*p* + 4*d*; Cl 1*s*–3*p* + 3*d*	14 953
	Cu 1*s*–4*p* + 4*d*; Cl 1*s*–3*p* + 4*s*, 4*p*	16 797
	Cu 1*s*–4*p* + 4*d*, 5*s*, 5*p*; Cl 1*s*–3*p* + 4*s*, 4*p*	16 986
	Cu 1*s*–4*p* + 4*d*, 5*s*, 5*p*; Cl 1*s*–3*p*	17 712
Ref. 39		16 870

* Actual potential fitted with atom-centred multipoles with $l \leqslant 1$. See text for details.

configurations. Already, calculations on d^1 chromium(V)[40] and vanadium(IV)[41] chlorides suggest comparable quantitative reproduction of at least the *d–d* spectra.

Conclusions

Discrete variational Xα self-consistent charge (DVXα s.c.c.) calculations of the *d–d* and c.t. spectra of five chlorocuprate complexes ($CuCl_n^{2-n}$, n = 4—6) have been undertaken. Highly accurate yet compact near-minimal atomic orbital basis sets have been generated for each molecule *via* a well defined procedure. With these optimised basis sets, the computed orbital-energy differences give better agreement with experimental *d–d* transition energies than other one-electron m.o. approaches. Transition-state calculations are found to be unnecessary for *d–d* spectra. For c.t. spectra on the other hand, transition-state calculations predict good splittings of the c.t. states but their absolute energies relative to the *d* manifold are in error by up to 10 000 cm^{-1}. This is probably due to a poor treatment of the Cl 3*p* orbital energy at the atomic (*i.e.* basis set) level.

The DVXα s.c.c. results are compared in detail with c.l.f. data. The descriptions of the nature of the metal-ligand interaction in terms of σ and π bonding are very similar providing due recognition is made that l.f.t. explicitly separates the *d* electrons from all others. The DVXα s.c.c. scheme is shown to be sensitive to the chemistry of these systems in that the correct assignments for the two $CuCl_6^{4-}$ complexes are only obtained when the calculations take into account that the axial ligands of one $CuCl_6^{4-}$ moiety are the equatorial ligands of neighbouring species.

Many of the suppositions of l.f.t. find independent quantitative confirmation in the DVXα s.c.c. calculations. Both approaches indicate that the *d* electrons are largely uncoupled from the rest but serve as useful 'probes' of the bonding-electron density. Furthermore, the *d*-orbital bases for all five complexes are shown to be essentially the same, quantitatively *via* the DVXα s.c.c. scheme and empirically *via* the c.l.f. model's 'sum rule.'

DVXα s.c.c. calculations in conjunction with c.l.f. analyses should therefore prove to be powerful tools for investigating the nature of metal–ligand bonding. The extension of this work to other systems will be the subject of future publications.

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