A Cellular Ligand-field Study of the $CuCl_4^{2-}$ Ion in $Cs_2[CuCl_4]$

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The ligand-field trace, Σ, expressed as the sum of local, diagonal ligand-field matrix elements, in earlier analyses of $Cs_2[CuCl_4]$ is shown to be anomalous when compared with those collected here for 26 complexes of copper(II), nickel(II), and cobalt(II). The present analysis shows how this anomaly may be removed when proper account is taken of the subtle details of the bonding and electron distribution in the distorted tetrahedral $CuCl_4^{2-}$ chromophore.

Recent ligand-field (l.f.) analyses[1,2] of the spectra of amino- and chloro-cuprates suggest that the sum (Σ) of cellular ligand-field (c.l.f.)* e_λ parameters is essentially independent of detailed molecular geometry and even co-ordination number. The quantity Σ, equal to the trace[4] of the molecular ligand-field matrix in the c.l.f. formalism, thus begins to provide a defensible basis for ligand-field parameter transferability between systems and hence to furnish a most useful guide for future l.f. analyses.

Results and Discussion

The Anomalous Ligand-field Trace in $Cs_2[CuCl_4]$.—Empirical measures of Σ for different metals and ligands so far indicate a widening field of application.[5,6] Meanwhile, Woolley[7] has recently examined the theoretical origin of the trace, showing how a residual spherical component of the ligand-field potential inevitably accompanies the natural parameterization scheme[8–10] of the c.l.f. However, our study[2] of chlorocuprates, in which $\Sigma \sim 23\,000$ cm^{-1} for octahedral and planar copper(II) species, gave the sum for the tetrahedral chromophore in $Cs_2[CuCl_4]$ as 33 200 cm^{-1}. The question arises, therefore, whether the Σ value for this tetrahedral complex is exceptional and whether a view can be formulated of the l.f. in this copper ion that is consistent with wider aspects of electron distribution and bonding.

Optimal and well established c.l.f. e_λ values and traces for both tetrahedral and octahedral amine and chloro complexes of copper(II) are collected in Table 1, together with those for some other metal(II) ions. Within the usual 5—10% accuracy of most l.f. analyses, all values quoted in Table 1 are uniquely determined. While Σ values are *ca.* 2 000 cm^{-1} larger for chloro than for amino complexes, for example, no real difference accompanies the change in co-ordination number, nor, from these data, the change in metal(II) ion. We shall consider this phenomenon in general and provide even more wide-ranging evidence of it in a later article. For the present, the exceptional position of the $CuCl_4^{2-}$ ion in $Cs_2[CuCl_4]$ is obvious: doubly so in view of the 'normality' of the trace in the *N*-benzylpiperazinium(1+) (Hbzpip) salt of the same ion (**2**). We also note the unexceptional trace of the tetrahedrally co-ordinated Cu^{II} ion in the cyclohexylamine complex, (**19**), and the similar sums for the six-co-ordinate imidazole and four co-ordinate, tetrahedral pyrazole complexes of Co^{II}, (**25**) and (**26**), respectively. Our original l.f. analysis[1] of $Cs_2[CuCl_4]$ yielded excellent reproduction of the experimental[11] transition energies and band assignments with unique c.l.f. e_σ and e_π values, so that our dissatisfaction with it now rests entirely upon this (equally unambiguous) observation of an anomalous value for the c.l.f. trace.

The Effect of Co-ordination Voids.—The first and obvious modification to consider is the inclusion of a l.f. contribution from the voids associated with the larger Cl–Cu–Cl angles (127 and 131°). The first of our recent series of analyses[1] has demonstrated the common occurrence of negative contributions to e_σ for co-ordinationally void sites in a complex. We also concluded that no such contribution was demonstrable in $Cs_2[CuCl_4]$, essentially because good reproduction of the experimental spectrum could be obtained without it. Furthermore, that conclusion was reached in the face of an earlier suggestion by Smith[12] that an (equivalent) such l.f. contribution may be present. Some support for our rejection of the void contribution, however, derives from our study[13] of the formally trigonal bipyramidal complexes $[Cu(bipy)_2I]I$ (bipy = 2,2′-bipyridine) and $[Cu(phen)(H_2O)][NO_3]_2$ (phen = 1,10-phenanthroline) which suggested that, while some negative l.f. contribution was evident opposite the equatorial water ligand in the phen complex (void angle 140°), none is apparent in the 120° void cell opposite the equatorial iodine donor in the bipy molecule. The essential irrelevance of any void contribution in the similarly sized (120°) void equatorial regions in a series[5] of metal(II) complexes of tris(*N*,*N*-dimethyl-2-aminoethyl)amine also confirms this position. So, at most, only a modest void contribution to the l.f. in $Cs_2[CuCl_4]$ could be expected. We find that inclusion of a non-zero value for e_σ(void) in the present analysis does indeed suggest a small value (-500 cm^{-1}), as shown by the parameter sets affording optimal fits to experiment:[11] Table 2, II. However, the corresponding trace, while smaller than before, is still unacceptably large and we must therefore look elsewhere if a consistent view of the l.f. in this complex is to be formed.

Non-cylindrical Cu–Cl *Bonding*.—There arises the possibility of a non-cylindrical Cu–Cl bonding due to the steric activity of the d^9 shell. This may be manifest both in anisotropic M–Cl π bonding and in so-called 'misdirected' M–L σ bonding. Consider first the π interactions. In exact T_d molecular symmetry, each Cu–Cl vector defines a three-fold axis: this, and the equal distribution of the hole in the d shell throughout the t_2 orbitals, ensures exact cyclindrical symmetry for any Cu–Cl π bond. Less obviously, we also expect virtually isotropic π bonding in planar $CuCl_4^{2-}$ ions. Here, the d-shell vacancy occurs in the $d_{x^2-y^2}$ orbital, each lobe of which is directed along a Cu–Cl vector. The repulsive role of the remaining, filled d orbitals will act to inhibit bond formation between metal p

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* The c.l.f. approach is exactly the same as the l.f. version of the angular overlap model that we have continuously espoused. Reasons for the change of name have been given recently.[3]

Table 1. C.l.f. e_λ values (cm^{-1}) and traces (cm^{-1}) in some four-, five-, and six-co-ordinated complexes of copper(II), nickel(II), and cobalt(II)

Complex[a]	Donor set[b]	e_σ(eq)	e_π(eq)	e_σ(ax)[c]	Σ[d]	Ref.
(1) $[PhCH_2CH_2NH_2Me]_2[CuCl_4]$[e]	Cl_4	5 300	900	−3 000	22 400	1
(2) $[Hbzpip]_2[CuCl_4]$[f]	Cl_4	5 200	900	−2 500	23 000	*g*
(3) $[Pt(NH_3)_4][CuCl_4]$	$Cl_4Cl'_2$	5 100	1 100	−2 050	25 100	2
(4) $[NH_3Pr^n]_2[CuCl_4]$	$Cl_4Cl'_2$	4 900	600	−750	22 900	2
(5) $[NH_3Et]_2[CuCl_4]$	$Cl_4Cl'_2$	4 737	455	−828	20 930	2
(6) $[NH_3Me]_2[CuCl_4]$	$Cl_4Cl'_2$	4 800	550	−600	22 400	2
(7) $[Cu(en)_2][BF_4]_2$	$N_4F'_2$	6 500	0	−2 750	20 500	1
(8) $[Cu(en)_2][SCN]_2$	$N_4S'_2$	6 500	0	−2 500	21 000	*g*
(9) $[Cu(en)_2][NO_3]_2$	$N_4O'_2$	6 375	0	−2 250	21 000	*g*
(10) $[Cu(en)_2Cl(OH_2)]Cl$	$N_4Cl'O'$	6 125	0	−1 750	21 000	*g*
(11) $[Cu(tach)_2][ClO_4]_2$	$N_4N'_2$	5 100	0	+700	21 800	1
(12) $[Cu(NH_3)_4][SCN]_2$	$N_4S'_2$	5 833	0	−1 317	20 698	1
(13) $[Cu(NH_3)_4][NO_2]_2$	$N_4O'_2$	5 700	0	−1 000	20 800	1
(14) $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]\cdot H_2O$	$N_4O'_2$	6 400	0	−2 800	20 000	1
(15) $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]\cdot NH_3$	$N_4N'_2$	5 800	0	−1 000	21 200	1
(16) $NH_4[Cu(NH_3)_5][PF_6]_3$	N_4N'	5 400	0	−750	20 850	1
(17) $[Cu(NH_3)_4(OH_2)]SO_4$	N_4O'	6 000	0	−4 500	19 500	*g*
(18) $[Cu(tren)(NH_3)][ClO_4]_2$	N_5	3 000	0	6 400	21 800	5
(19) $[Cu(NH_2C_6H_{11})][NO_3]_2$	N_4	6 350	0	−2 300	20 800	*g*
(20) $[Ni(NH_3)_6][ClO_4]_2$	N_6	3 667	0		22 000	6
(21) $[Ni(en)_3)][NO_3]_2$	N_6	4 075	0		24 450	6
(22) $[Ni(pn)_3][NO_3]_2$	N_6	3 830	0		22 980	6
(23) $[Co(en)_3][NO_3]_2$	N_6	3 800	0		22 800	*h*
(24) $[Co(oabi)_3]S_2O_6\cdot H_2O$	N_6	4 100	0		24 600	*h*
(25) $[Co(Him)_6][NO_3]_2$	N_6	3 800	275		24 450	*g*
(26) $[Co(tdmpea)][BPh_4]_2$	N_4	5 200—	900—	4 100—	22 400—	*j*
		3 200[i]	2 900[i]	6 100[i]	24 400	

Statistics:[k]	$\overline{\Sigma}$	Standard deviation
$Cu(Cl_4)$	22 788	1 353
$Cu(N_4X_2)$	20 842	625

[a] Abbreviations: en = 1,2-diaminoethane, tach = 1,3,5-triaminocyclohexane, tren = tris(2-aminoethyl)amine, pn = propane-1,2-diamine, oabi = 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane, Him = imidazole, tdmpea = tris[2′-(3,5-dimethylpyrazolyl)ethyl]amine. [b] Primed donors occupy axial sites at long distances. [c] e_σ(ax) values refer to each co-ordination void in planar species, to the sum of axial ligand and void in square pyramidal, five-co-ordinate molecules, or to axially co-ordinated ligands as normal. [d] $\Sigma \equiv \sum^{\text{ligands}} (e_\sigma + e_{\pi x} + e_{\pi y})$. [e] Planar chromophore. [f] Large Cl–Cu–Cl angles (167°). [g] R. J. Deeth and M. Gerloch, unpublished results. [h] C. A. Brown, M. Gerloch, and R. F. McMeeking, unpublished results. [i] e_λ Values describe ranges of good fit to the spectrum. [j] A. R. Dale and M. Gerloch, unpublished results. [k] Primary donors given in parentheses.

Table 2. Optimal c.l.f. parameter sets (cm^{-1}) for $Cs_2[CuCl_4]$

Model	e_σ	$e_{\pi x}$	$e_{\pi y}$	$e_{\pi\sigma}$	e_σ(void)	Σ	Remarks
I	5 600	1 350	1 350	0	0	33 200	Original analysis
II	5 200	1 050	1 050	0	−500	28 200	Include void
III	4 975	75	700	0	0	23 200*	Anisotropic e_π
IV	5 400	1 200	1 200	50	0	31 200	Maximum $e_{\pi\sigma}$
V	4 840	160	750	50	0	23 000*	$e_{\pi\sigma}$ + anisotropic e_π
VI	5 000	700	800	0	−400	25 200*	e_σ(void) + anisotropic e_π
VII	4 475	950	750	200	−850	23 000*	Void + $e_{\pi\sigma}$ + anisotropic e_π

* Selected as optimal from ranges given in Table 3.

orbitals and ligand functions but will be essentially cylindrically symmetric with respect to each local Cu–Cl vector. Now consider the situation in the distorted tetrahedral geometry of the $CuCl_4^{2-}$ ion in the cesium salt. The $d_{x^2-y^2}$ orbital (referred to the planar situation; or d_{xy} in the usual tetrahedral reference frame) still houses the hole, nearly completely, because of its large energy separation (*ca.* 5 000 cm^{-1}) from any other orbital in this ion. However, the Cu–Cl vector is now inclined with respect to the local lobe of the hole, as shown in Figure 1, and we no longer expect $e_{\pi x} \sim e_{\pi y}$. If the aspherical occupancy of the d^9 shell is indeed reflected in unequal e_π parameter values, we must simultaneously entertain the possibility of some degree of misdirected Cu–Cl σ bonding also. While being unable to quantify the effect, it seems reasonable to expect that the lesser repulsion of the $d_{x^2-y^2}$ hole lobe will encourage better σ overlap of metal *s* and *p* functions with Cl σ orbitals in the (exaggerated) bent manner shown in Figure 2. Within the c.l.f. approach, this situation is represented by the inclusion of a non-zero, locally off-diagonal matrix element of the cellular potential, $e_{\pi\sigma} \equiv \langle d_{z^2}|V_{\text{l.f.}}|d_{xz}\rangle$, as described elswhere.[5,14]

A Composite Approach.—Altogether, therefore, we are led to consider three 'refinements' of the basic parameterization scheme in $Cs_2[CuCl_4]$ involving contributions to the l.f. from anisotropic π bonding ($e_{\pi x} \neq e_{\pi y}$), bent σ bonding ($e_{\pi\sigma} \neq 0$), and from the ligand-free but not electron-free space subtended

Table 3. Ranges of acceptable c.l.f. parameters (cm^{-1}) for $Cs_2[CuCl_4]$ for various models

e_σ	$e_{\pi x}$	$e_{\pi y}$	$e_{\pi\sigma}$	e_σ(void)	Σ	Remarks
4 500	−700	200	0	0	16 000	Anisotropic e_π
5 600	1 200	1 400	0	0	32 800	
4 200	−1 100	−100	50	0	12 000	Anisotropic e_π and $e_{\pi\sigma} = 50$
5 350	950	1 300	50	0	30 400	
5 000	700	800	0	−400	25 200	Anisotropic e_π and e_σ(void) = −400
6 100	2 700	2 000	0	−400	42 400	
4 200	−100	400	200	−500	17 000	Anisotropic e_π + e_σ(void) + $e_{\pi\sigma}$
5 000	2 800	1 400	200	−500	33 800	

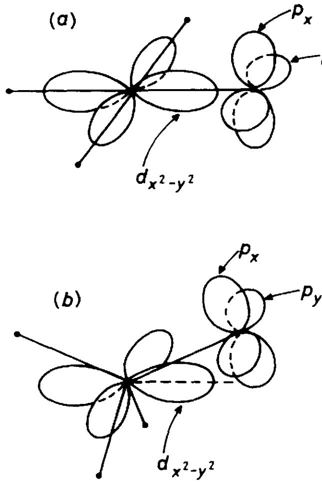

Figure 1. Near-cylindrical Cu–Cl bonding expected in the planar $CuCl_4{}^{2-}$ ion where the chlorine ligand lies on the axis of the $d_{x^2-y^2}$ hole lobe. (b) Anisotropic Cu–Cl bonding anticipated in the distorted tetrahedral $CuCl_4{}^{2-}$ ion of $Cs_2[CuCl_4]$; π donation from p_x is expected to be enhanced in the presence of the $d_{x^2-y^2}$ hole lobe

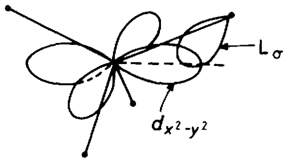

Figure 2. The lesser repulsion of the $d_{x^2-y^2}$ hole, which is expected to encourage a degree of 'misdirected' Cl donation and overlap with the Cu s and p orbitals; L_σ = ligand σ orbital

by the larger Cl–Cu–Cl angles [e_σ(void) < 0]. As we demonstrate below, our ultimate view of the bonding and l.f. in this complex does indeed incorporate all three contributions. However, we arrive at that conclusion best by consideration of these effects initially in isolation and then in co-operation, as follows.

First we explore the effect of unequal e_π parameters. Unfortunately, even with four transition energies available to establish values for the three parameters, e_σ, $e_{\pi x}$, $e_{\pi y}$, 'best fit' correlations are evident, and are summarized in Table 3. Nevertheless, it is clear that an acceptable value for Σ (*ca.* 23 000 cm^{-1}) is now attainable, though with a marked anisotropy in the Cu–Cl π parameters. However, not only is the extent of this anisotropy disquieting but its sign is inconsistent with the local electronic environment. Thus, we observe from Figure 1 how the attractive (*i.e.* less repulsive) lobe of the $d_{x^2-y^2}$ hole orbital now favours stronger donation from the Cl atom in the vertical plane (local x), with little change expected in the horizontal: in short, we anticipate $e_{\pi y} < e_{\pi x}$. Hence a chemically consistent l.f. analysis is not provided by the 'best' entry III in Table 2.

Now consider simultaneous contributions from anisotropic parameters and a non-zero e_σ(void). Again, correlated best-fit parameter values are obtained (Table 3) but we emphasise that the chemical and l.f. consistency we seek are acceptable even when not unique: we merely argue for the elimination of alternatives here. The ranges quoted throughout the correlation of Table 3 represent regions of subjectively acceptable fit with experiment. It is apparent that the combination of anisotropic e_π and non-zero e_σ(void) parameter values is promising where their separate effects were not. A lowered trace value and a sensibly small anisotropy in parameters in the sense $e_{\pi x} > e_{\pi y}$ are obtainable. However, the best that can be achieved from the combination is, as shown in Table 2, still less than ideal so far as the trace Σ is concerned.

Turning to the effects of misdirected σ bonding, in $Cs_2[CuCl_4]$, calculated transition energies are especially sensitive to the $e_{\pi\sigma}$ parameter, and the maximum value it can take while still yielding good reproduction of the experimental spectrum is *ca.* 50 cm^{-1}. As shown for IV in Table 2, the associated value of Σ is still unacceptably high. However, inclusion of a non-zero $e_{\pi\sigma}$ value without anisotropic e_π values is hardly defensible. Simultaneous consideration of both contributions again yields widely correlated fits (Table 3) and although acceptable Σ values can be achieved, that is so only in association, once more, with anisotropic e_π values in the 'wrong' sense.

Conclusions

We are led to include l.f. contributions of all three kinds: anisotropic e_π, off-diagonal $e_{\pi\sigma}$, and e_σ(void). It is physically reasonable to take these effects together and so combine views of the electron distribution in complexes that have been established in other contexts.[1,5,14] Wide correlations between best-fit c.l.f. values inevitably accompany so wide a parameterization scheme and the range given in Table 3 only represents the general situation. Similarly, the optimal set in Table 2 for VII is not unique but given merely to show how a consistent view, both qualitative and quantitative, is possible. The trace has been fixed at 23 000 cm^{-1} in line with values in Table 1; the anisotropy in e_π is modest and in the comprehensible sense $e_{\pi x} > e_{\pi y}$; only small values for $e_{\pi\sigma}$ and e_σ(void) are necessary.

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