Charge Density and Spectra of Dichlorotetrakis(thiourea)nickel(II): An *Ab Initio* Discrete Variation Xα Calculation

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An *ab initio* calculation using the discrete variational Xα implementation of Hartree–Fock–Slater theory, with frozen cores, has been performed on the compound [Ni(tu)$_4$Cl$_2$] (tu = thiourea) in the experimental geometry, and the results compared with the optical spectra, the magnetic susceptibilities, and the charge-density distribution. The treatment provides a better account of the experimental observations than earlier analyses using empirical ligand-field models. It suggests a reassignment of some features of the spectra, and supports the quite appreciable covalence, involving both σ- and π-charge flows, that is observed in the charge-density study. The reduction in the electron-repulsion parameters inferred in our interpretation of the spectra is consistent with this large covalence.

Dichlorotetrakis(thiourea)nickel(II), [Ni(tu)$_4$Cl$_2$], has been used, together with the other members of the series [M^{II}(tu)$_4$Cl$_2$], as an example of the effects on metal–ligand bonding of a tetragonal distortion from octahedral symmetry.[1–5] The crystal structure[6–8] of the compound contains six-co-ordinated nickel(II) and each molecule has two *trans* chlorine ligands, collinear along the crystal *c* axis, and four thiourea (tu) molecules co-ordinated almost, but not quite, in a square plane perpendicular to *c*. The overall molecular site symmetry is non-centrosymmetric C_4. The four tu molecules are all related by symmetry but the two Cl atoms are independent, with Ni–Cl bond lengths of 240.2(2) and 250.0(2) pm at 140 K.[8]

The optical spectrum of the compound at room temperature and the temperature dependence of its magnetic susceptibility were initially interpreted by Hare and Ballhausen[2] using a weak crystal-field model. In the spectrum the three bands typical of octahedral nickel(II) complexes, $^3A_{2g} \longrightarrow {}^3T_{2g}$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$ occur at frequencies appropriate for the positions of the Cl and tu ligands in the spectrochemical series. The polarised spectra show rather indistinct frequency shifts compatible with a difference in ligand-field strengths (Cl > tu), leading to a tetragonal splitting of bands. Gerloch *et al.*[3] remeasured the optical spectrum at 5 K and also obtained the anisotropic magnetic susceptibilities. From the zero-field splitting parameter obtained from the magnetic data they inferred, assuming a spin-orbit coupling of the ground term only with the $^3T_{2g}$ term, that the ligand-field effects are in the order tu > Cl. The remaining data fit satisfactorily to a simple crystal-field model (*Dq*, *Ds*, *Dt*, and k[9]), although as is usual in such models the parameter/observation number ratio is not good.

Figgis and Reynolds[8] measured the deformation charge density in a crystal of [Ni(tu)$_4$Cl$_2$], and showed, *inter alia*, that the chlorine atom donates more charge to the nickel atom than the thiourea molecule. This fact was rationalised with the contrary order inferred from the spectra[3] by noting the different effects orbital energies and overlap each have on charge transfers and energy levels.

However some doubts remain over the situation. First, the overlap and the orbital energies required to explain both diffraction and spectral data, while not unreasonable, are at the borderline of acceptable values. Secondly, the simple method of inferring the separation of the components of the lowest spectra band from the zero-field splitting parameter often fails. In the cases of the [CoCl$_4$]$^{2-}$ ion in Cs$_3$CoCl$_5$,[10] Cr^{3+} doped in Al$_2$O$_3$,[11] and the [FeCl$_4$]$^-$ ion[12] for example there is clear experimental evidence that the splitting of the lowest band is of the *opposite* sign to that predicted from the zero field splitting and an ionic model with crystal-field splittings. The failure appears to be connected to the significant effect of all the other terms of the complete *d* manifold in addition to the lowest term[13] and to differences in the covalence interaction of the *d* orbitals of the metal atom with the ligands.[12] Thirdly, the assignment of some bands as *d–d* in the covalent model [Ni(NH$_3$)$_4$(NO$_2$)$_2$], also with tetragonal donor atom symmetry, has been strongly questioned, making a ligand-field interpretation of the spectrum misleading without further information.[14] Lastly, the use of ligand-field models in a system with significant covalence has severe limitations.

An *ab initio* calculation may throw light on these questions. Recently the discrete variational Xα (DV-Xα) method has been shown to predict spectroscopic data for a number of simple transition-metal complexes,[15,16] and provides in some cases an alternative to the empirical angular overlap and cellular ligand field methods of accounting for the spectra. We present here a DV-Xα calculation for [Ni(tu)$_4$Cl$_2$], and compare the results with the spectra and with the charge-density results.

Calculations

The DV-Xα method has been used over a wide area of chemistry (see for example ref. 12 and refs. therein) so only an outline is presented here. DV-Xα calculations of the wavefunction for a molecule in experimental geometry, as currently implemented, require only two assumptions. First, that the wavefunction is of single determinantal nature, and secondly, the usual Xα approximation, that the non-local exchange-correlation term can be replaced by the local Hartree–Fock–Slater term.[17] Other assumptions used previously in the implementation of the local-density approximation, for example the 'muffin-tin'[18] and the self-consistent charge[19] potentials, are not necessary in the version employed here, partly because it employs numerical rather than analytic basis sets. With sufficient integration points, and sufficient multipoles used in the fitting of the potential, the only serious remaining error lies in the quality of the basis sets.[20]

We have used as basis sets a single numerical function per valence orbital, obtained by numerical solution of the Hartree–Fock–Slater equations for the atoms or ions. In obtaining those functions it is useful to confine the atom in a potential well to

Table 1. Eigenvalue data for [Ni(tu)$_4$Cl$_2$] between −8 and 0 eV (1 eV ≈ 1.60 × 10^{-19}J). Content is noted if any nickel orbital coefficients are greater than 0.2

Orbital	Symmetry	Spin	*E*/eV	Content	Coefficient
87	11*B*	+	−7.914 9	part $3d_{x^2-y^2}$	0.66
88	11*E*	+	−7.793 5	part $3d_{xz,yz}$	0.37
90	14*A*	+	−7.754 6	part $3d_{z^2}$	0.56
91	11*E*	−	−7.622 6		
93	15*A*	+	−7.297 6		
94	14*A*	−	−7.270 7	part $3d_{z^2}$	0.29
95	11*B*	−	−7.219 6	part $3d_{x^2-y^2}$	0.49
96	15*A*	−	−7.048 2	part $3d_{z^2}$	0.39
97	12*E*	+	−7.042 4		
99	12*B*	+	−7.002 0	part $3d_{xy}$	0.65
100	13*E*	+	−6.987 1	part $3d_{xz,yz}$	0.65
102	12*E*	−	−6.887 4		
104	13*E*	−	−6.527 7	part $3d_{xz,yz}$	0.31
106	12*B*	−	−6.512 3	part $3d_{xy}$	0.25
107	14*E*	+	−6.413 4		
109	14*E*	−	−6.296 0		
111	16*A*	+	−6.152 4		
112	13*B*	+	−6.073 3	part $3d_{xy}$	0.70
113	16*A*	−	−6.044 6		
114	15*E*	+	−6.028 8	part $3d_{xz,yz}$	0.64
116	15*E*	−	−5.036 2	most $3d_{xz,yz}$	0.91
118	13*B*	−	−4.965 6	most $3d_{xy}$	0.92
119	17*A*	+	−4.877 8	most $3d_{z^2}$	0.72
120	14*B*[a]	+	−4.862 4	most $3d_{x^2-y^2}$	0.64
121	14*B*[b]	−	−4.008 1	most $3d_{x^2-y^2}$	0.77
122	17*A*	−	−3.847 5	most $3d_{z^2}$	0.84
123	16*E*	+	−3.385 1	most $4p_{x,y}$	0.76
125	16*E*	−	−3.215 0	most $4p_{x,y}$	0.75
127	17*E*	+	−2.847 7		
129	17*E*	−	−2.828 5		
131	15*B*	+	−2.761 5		
132	15*B*	−	−2.713 0		
133	18*A*	+	−2.675 4		
134	18*A*	−	−2.632 3		
135	18*E*	+	−1.763 9		
137	18*E*	−	−1.730 8		
139	19*A*	+	−1.218 8		
140	19*E*	+	−1.193 7		
142	19*A*	−	−1.184 1		
143	16*B*	+	−1.170 5		
144	19*E*	−	−1.169 9		
146	16*B*	−	−1.132 2		

[a] Highest occupied molecular orbital. [b] Lowest unoccupied molecular orbital.

limit the extent of the diffuse bases, but taking care that occupied orbitals are not significantly changed. This basis set contains atomic-basis functions each of about double-zeta quality. However these atomic functions, while accurate for the atoms, are not sufficiently flexible for molecular calculations of the highest accuracy. The near doubling of the basis set required to obtain such flexibility makes such a calculation on [Ni(tu)$_4$Cl$_2$] beyond our computing resources at present.

For Ni^{2+} we have functions 1*s*—4*f*, for Cl and S 1*s*—3*d*, inclusive, for C and N 1*s*—2*p* plus 3*d*, and for H 1*s* plus 2*p*. The atomic cores (Ni 1*s*—3*p*, S and Cl 1*s*—2*p*, and C and N 1*s*) were frozen in the calculation. 8 980 Integration points were employed. The coulomb potential was fitted with multipoles up to order 2, these values being sufficiently large as to produce negligible errors associated with the numerical calculation. The experimental geometry at 140 K[8] was employed.

We used the unrestricted Hartree–Fock (UHF) formalism since it is known both experimentally[21] and theoretically[22] that the complete neglect of electron–electron correlation inherent in the restricted method produces unacceptable errors in many calculated properties. The main calculation of the series reported here occupied *ca.* 9 h of cpu time on a SUN 380S workstation. A list of the calculated eigenvalues near the Fermi level, with notes on the associated eigenvector, are given in Table 1. The Xα eigenvalues, unlike those from conventional Hartree–Fock procedures, do not give energy differences directly for comparison with optical absorption bands.[17] Ideally a transition-state calculation for each energy difference should be made, but that would be a lengthy process. The differences are not expected to be significant for metal-centred transitions, so we have restricted ourselves to ground-state eigenvalue differences in this work.

This Xα calculation is effectively a strong-field one in the ligand-field sense, in that the effect of electron–electron repulsion in repopulating *d* orbitals to give non-integral populations is neglected. Nickel(II) complexes such as [Ni(tu)$_4$Cl$_2$] are traditionally described in the weak ligand-field regime, which is certainly appropriate in rather ionic species such as [Ni(H$_2$O)$_6$]$^{2+}$. To recover the weak-field results from the Xα calculation properly, we would need to perform configuration-interaction calculations. For the ground $^3A_{2g}$ and excited $^3T_{2g}$ terms in O_h symmetry for the $3d^8$ configuration this is unnecessary as these states correlate with a single strong-field configuration. The $^3T_{1g}$ terms mix different strong-field configurations, and so transitions to these states are not simple to calculate. Fortunately the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition is the lowest and also the one which is most important in deciding on the difference between the effects of the thiourea and the chlorine ligands.

Electronic transitions within the thiourea molecule commence around 26 000 cm^{-1}. Transitions at lower frequencies arise from molecular orbitals with substantial metal content in both the ground and the excited states. We consider only spin-allowed (triplet ⟶ triplet) transitions with significant metal–metal overlap, and we worked within the strong-field approximation. In C_4 symmetry, 'parallel' (to the *c* axis) electric-dipole allowed absorption bands arise from $^3B \longrightarrow {}^3B$ and 'perpendicular' bands from $^3B \longrightarrow {}^3E$ transitions[2] and we consider only those. Both these approximations are rather severe, and neglect vibronic coupling as a source of intensity. However Ballhausen[23] has noted that in non-centrosymmetric point groups, as here, 'a great part of the band intensity turns out to be electric dipole.' The predicted band frequencies are listed in Table 2, together with an interpretation of the observed spectra. As Gerloch *et al.* imply,[3] peak existence, let alone assignment, is subjective in these rather featureless spectra.

Table 3 lists some pertinent charge density data, which are compared with the experimental results.

Discussion

Charge and Spin Density.—The present calculation shows both σ- and π-charge donation from the chlorine atoms into metal $3d_{z^2}$ and diffuse orbitals, and also donation from the thiourea molecules into the metal orbitals, accompanied by spin transfer, almost exclusively by σ effects, into the ligand orbitals. This is just the behaviour expected from a $t_{2g}{}^6e_g{}^2$ ion, where the spin resides in the e_g orbitals. The amount of covalence is quite large, the nickel atom, for example, is calculated to transfer 36% of its spin to the ligands.

Table 2. Optical spectra (cm^{-1}) of [Ni(tu)$_4$Cl$_2$] below 27 000 cm^{-1}, with predictions from the present calculation in the strong-field approximation. s = strong, m = medium, w = weak, v = very, and sh = shoulder

Parallel ($^3B \longrightarrow {}^3B$)		
Transition	Calculated	Observed
		6 500(?)w
$13B- \longrightarrow 14B-$	7 725 $3d \longrightarrow 3d$	7 500w
		10 500(?)vw
$12B- \longrightarrow 14B-$	20 204 ligand $\longrightarrow 3d$	
$15E+ \longrightarrow 16E+$	21 329 $3d \longrightarrow 4p$	22 000s
$15A- \longrightarrow 17A-$	25 823 ligand $\longrightarrow 3d$	
$11B- \longrightarrow 14E-$	25 911 ligand $\longrightarrow 3d$	
$13E- \longrightarrow 16E-$	26 725 ligand $\longrightarrow 3d$	

Perpendicular ($^3B \longrightarrow {}^3E$)		
Transition	Calculated	Observed
		6 500(?)w
$15E- \longrightarrow 14B-$	8 295 $3d \longrightarrow 3d$	7 500w
$15E- \longrightarrow 17A-$	9 590 $3d \longrightarrow 3d$	9 300w
		10 500w
$14B+ \longrightarrow 16E+$	11 919 $3d \longrightarrow 4p$	12 300 (sh)
$17A+ \longrightarrow 16E+$	12 043 $3d \longrightarrow 4p$	
$15E- \longrightarrow 16E-$	14 693 $3d \longrightarrow 4p$	13 600m
$13B- \longrightarrow 16E-$	14 123 $3d \longrightarrow 4p$	13 500s
		16 000w
$13B- \longrightarrow 15E-$ $14B- \longrightarrow 17B-$	17 315 $3d \longrightarrow 3d$	18 000w
$13E- \longrightarrow 14B-$	20 328 ligand $\longrightarrow 3d$	20 000 (sh)
$13E- \longrightarrow 17A-$	21 623 ligand $\longrightarrow 3d$	
$13B+ \longrightarrow 16E+$	21 688 $3d \longrightarrow 4p$	22 400s
$12B- \longrightarrow 16E-$	26 602 ligand $\longrightarrow 4p$	

Table 3. Selected populations and charge- and spin-transfers in [Ni(tu)$_4$Cl$_2$]

	Charge		
Transfer	Calculated	Observed	Spin calculated
tu $\longrightarrow$ Ni	0.169	0.17(20)	−0.147
Cl(1)σ $\longrightarrow$ Ni	0.123	mean	−0.117
Cl(2)σ $\longrightarrow$ Ni	0.251	0.16(14)	−1.124
Cl(1)π $\longrightarrow$ Ni	0.026	mean	0.003
Cl(2)π $\longrightarrow$ Ni	0.128	0.35(15)	0.009
Cl(1)δ $\longrightarrow$ Ni	0.036	—	0.001
Cl(2)δ $\longrightarrow$ Ni	0.002	—	0.000
Population			
Ni: $3d_{z^2}$	1.31	1.32(14)	0.64
$3d_{xz,yz}$	3.90	3.08(18)	0.01
$3d_{x^2-y^2}$	1.40	1.12(14)	0.62
$3d_{xy}$	1.91	1.91(14)	0.01
Diffuse	0.73	2.2(3)	−0.07

The calculation shows that the average chlorine charge donation is almost twice that from each thiourea sulphur atom, and has a significant π component. This observation is consistent with the charge-density experiment. The nickel atom configuration, with e_g populations exceeding unity and those of t_{2g} orbitals reduced from 2.00 each, and with a substantial diffuse component, also agrees with the charge-density experiment. However the experimentally observed $3d_{xz,yz}$ population is high (5σ level) compared with the calculation.

Comparison of the calculated charge and spin densities shows that spin transfers are consistently less than the charge transfers. This phenomenon is a result of electron–electron correlation in which formally spin-paired orbitals adjust their spatial dependence so as to concentrate more spin on the spin-rich metal centre, thus reducing the net transfer to the ligands. This spin-polarisation effect has been observed elsewhere consistently, both experimentally and in theoretical calculations which include electron–electron correlation.[21]

Optical Spectra.—Weak-field interpretation. We reiterate the essence of the interpretation by Gerloch *et al.*[3] The two most intense spectral bands in [Ni(tu)$_4$Cl$_2$] at *ca.* 13 500 and *ca.* 22 000 cm^{-1} correspond to the O_h symmetry transitions $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$. Using a Tanabe–Sugano formalism[24] this gives Dq 8 300 cm^{-1} and B 730 cm^{-1}, where Dq is the conventional cubic ligand-field parameter and B is one of the Racah parameters of interelectronic repulsion. These parameters predict the $^3A_{2g} \longrightarrow {}^3T_{2g}$ band at 8 300 cm^{-1} and the $^3A_{2g} \longrightarrow {}^1E_g$ spin-forbidden band often observed in Ni^{2+} complexes at 11 680 cm^{-1}. The sharp band observed at 10 500 cm^{-1} is assigned as the latter. The two bands observed at 7 500 and 9 300 cm^{-1} are assigned to the transition to the tetragonally split $^3T_{2g}$ term, and are then $^3B \longrightarrow {}^3E$ and $^3B \longrightarrow {}^3B$ if this simply based argument is accepted.

While this provides a satisfactory explanation, there are a number of points for concern, apart from the assignment of the two lowest peaks, already discussed. The two peaks at 13 600 and 22 000 cm^{-1} in the parallel spectrum are electric-dipole forbidden, yet are observed as being rather intense. The corresponding perpendicular peaks are also very intense. Hare and Ballhausen[2] note that these intensities are larger than those observed in six-co-ordinated nickel(II) complexes with similar values of 10 Dq, and infer that there is an enhancement of intensity due to the lack of a centre of symmetry. Presumably the origin of the extra intensity is in the electric dipole rather than the vibronic mechanism; see the discussion in ref. 22. However this explanation is incompatible with the observed polarisation properties of the bands. Also there is the question of the observed values for the Racah B parameters. These are affected by covalence, varying perhaps as the fourth power of the coefficients in the relevant molecular orbitals. For the $^3A_{2g} \longrightarrow {}^1E_g$ transition both terms are of $t_{2g}{}^6e_g{}^2$ origin and we expect a transition energy of $16B$. The situation is satisfactory, as the observed reduction in B from the free-ion value of *ca.* 1 060 to 656 (10 500/16) cm^{-1} implies an 'average' $3d$ coefficient of 0.89 in the orbitals $15E-$ and $13E-$, and that is just what is found. However, for $^3A_{2g} \longrightarrow {}^3T_{1g}$ we predict a value of B of *ca.* 570 (1 060 × 0.8^2 × 0.92^2) rather than the observed 730 cm^{-1}.

Covalence, by diluting the $3d$ participation in individual molecular orbitals also removes some of the effect of electron–electron repulsion, for example by mixing the T_{1g} terms, as also does the reduction in symmetry. This compound, even though of the first transition series, may be sufficiently covalent and of low enough symmetry that a strong-field interpretation of the spectrum may reveal useful features.

Strong-field interpretation. The most intense features of both the parallel and the perpendicular spectra are the bands at *ca.* 13 500 and *ca.* 22 000 cm^{-1}. These correspond to calculated transitions $3d \longrightarrow 4p$ which are electric-dipole allowed in atomic spectroscopy, and so might be expected to be intense for molecular orbitals involving substantial $3d$ and $4p$ components. The perpendicular spectrum has a distinct shoulder that is probably absent in the parallel spectrum. Again it can be assigned to a transition involving a change from $3d$ to $4p$ character. Other transitions are formally forbidden ($3d \longrightarrow 3d$) or only begin to appear in quantity above *ca.* 26 000 cm^{-1} ($3d \longrightarrow$ ligand). We note that this electric-dipole allowed $3d \longrightarrow 4p$ transition is permitted in both parallel and perpendicular spectra, as is observed.

If we look in more detail we see that the maxima of the two intense peaks are slightly different in the parallel and the perpendicular spectra, and in the senses that the calculation predicts. These transitions both involve b and e orbitals split by the tetragonal component of the ligand field. Our definition of tetragonality here is in the same sense as that used by Hare and Ballhausen [2] in their ligand-field model, and opposite to that of the earlier analysis of the spectra.[3] In between these two bands a number of ill defined peaks are observed, perhaps at 16 000, 18 000, and 20 000 cm^{-1} in the perpendicular polarisation. There is a predicted $3d \longrightarrow 3d$ ($t_{2g}{}^6e_g{}^2 \longrightarrow t_{2g}{}^4e_g{}^4$) band at 17 300 cm^{-1} and some mainly ligand to $3d$ bands at 20 000 cm^{-1} in the perpendicular spectrum and 20 204 cm^{-1} in the parallel spectrum, but no definite assignment can or should be made. All other features of interest are below 12 000 cm^{-1}.

There are three possible single-excitation *d–d* transitions predicted and observed, two in perpendicular and one in parallel polarisation. The transitions at 7 725 ($\|$) and 8 295 ($\perp$) cm^{-1} arise from a π splitting of the t_{2g} orbitals ($3d_{xy}$ and $3d_{xz,yz}$) of 570 cm^{-1}. The splitting observed in the experimental spectrum is not significant. The transitions involving the e_g orbitals ($3d_{z^2}$ and $3d_{x^2-y^2}$) split by σ bonding are the bands at 8 295 ($\perp$) and 9 590 ($\perp$) cm^{-1}. The observed splitting, 1 800 cm^{-1}, compares quite well with the calculated value, 1 295 cm^{-1}. The sign of the calculated splitting implies that Cl has a greater ligand-field effect than has tu. The opposite assignment, and relative strengths of ligand field, used earlier,[3] cannot definitely be discounted on the basis of the optical spectra alone. However, for σ splitting greater than π (as calculated and observed), the absence of a parallel forbidden $^3B \longrightarrow {}^3A$ ($13B- \longrightarrow 17A-$) peak at *ca.* 9 300 cm^{-1} assigns the 9 300 cm^{-1} perpendicular peak as $15E- \longrightarrow 17A-$ and that at 7 500 cm^{-1} as $15E- \longrightarrow 14B-$, in agreement with the order of ligand-field strength (Cl > tu). For the assumption that tu > Cl we would expect, in the parallel spectrum, a peak at *ca.* 9 000 cm^{-1} and no peak at *ca.* 7 500 cm^{-1}. However, we should be careful not to place too much reliance on the absence of a peak in such an ill defined spectrum. The above is weak evidence, but again it leads in a consistent direction Cl > tu in ligand-field strength.

The last observed feature unexplained is the sharp peak at 10 500 cm^{-1}. Weak-field methods assign this band to a spin-forbidden transition, involving a change in electron–electron repulsion within a $t_{2g}{}^6e_g{}^2$ configuration. We notice in Table 1 that metal-centred +spin orbitals are shifted markedly in energy relative to spatially similar −spin orbitals. This is a consequence of the unrestricted Hartree–Fock approximation which includes not only electron repulsion in the Hartree–Fock time-averaged way but also includes part of its effect on electron–electron correlation. Since the latter changes dramatically for triplet ⟶ singlet transitions we expect our calculation to be poorer than for triplet ⟶ triplet transitions where any correlation errors at least partly cancel. From Table 1 we calculate *d–d* peaks at 6 893 and 8 312 and $3d \longrightarrow 4p$ at 13 321 cm^{-1} for the parallel, and $3d \longrightarrow 4p$ at 12 751, 13 291, and 13 415 cm^{-1} for the perpendicular case. We tentatively assign the peaks at 10 500 cm^{-1} to a $3d \longrightarrow 4p$ spin-forbidden transition, since the parity change makes it more allowed than a $3d \longrightarrow 3d$ transition. The possible peaks at 6 500 cm^{-1} need more experimental work to determine their existence and origin before we can assign them to spin-forbidden $3d \longrightarrow 3d$ transitions.

A final point to be made is that these assignments have shifted the $^3B \longrightarrow {}^3E(T_{1g})$ transition down in energy markedly compared to the weak-field assignment. Together with the $^3B \longrightarrow {}^3E(T_{2g})$ transition they outweigh the effect of $^3B \longrightarrow {}^3B$ on the ground state, so that in spite of the latter being calculated to be almost equal in energy to $^3B \longrightarrow {}^3E(T_{2g})$, the sign of the observed splitting is as predicted. A surprising feature of these comparisons is that the very crude method of selecting observable transitions seems to work.

Conclusion

The present DV-Xα calculation explains both the charge density and optical spectra well. Such calculations are relatively easy to implement and, while moderately demanding of computing resources, they are within the compass of a typical engineering-oriented workstation. They may thus become a useful routine tool in these fields.

In this particular case it appears that covalence is so strong that a strong-field calculation of the optical spectrum produces a more satisfactory agreement than does a weak-field one. The strong-field approximation gives a much better prediction of both the number, intensity, and polarisation dependence observed, excepting only the single observed triplet ⟶ singlet transition. The good agreement is also probably due to the non-centrosymmetric low-site symmetry which permits electric-dipole allowed intensity to dominate the spectrum, in place of the more difficult to calculate vibronically induced intensity more normally seen in Ni^{2+} complexes.

The calculation predicts that chlorine exerts a slightly stronger ligand-field effect than does thiourea. The reassigned spectra and simple interpretation of the zero-field splitting parameter now agree with this conclusion. This reassignment increases *Dq* for chlorine substantially as required, and in addition, within the framework of a Wolfsberg–Helmholz model,[8] makes the overlap and energy parameters for chlorine and thiourea much more similar to each other, and thus more believable. Perhaps the strongest evidence that the calculation is correct, and that the spectra should indeed be reassigned, is a chemical one; comparison with other complexes. It was observed[3] that the earlier assignment produces a '*Dq*' for chlorine that is low compared with other complexes and that in related cases chlorine does have a larger effect than thiourea.

More generally, this study illustrates the utility of diffraction experiments. The charge density is sufficiently accurate, if only just so, to provide a useful test of the theoretical calculation, and thus prompt a reassignment of the spectroscopic results. Conversely, doubt has again been thrown on the reliability of the simple relation of zero-field splitting parameters to other properties. Spin-density distributions, from polarised neutron diffraction experiments, can provide data on covalence about 10 times more precise than do charge-density studies from *X*-ray diffraction and would thus provide a much more stringent test of this and other wavefunctions (*cf.*, Table 3). However, the non-centrosymmetric unit cell of $[Ni(tu)_4Cl_2]$ would make the interpretation of a polarised neutron diffraction experiment on it a challenge, for technical reasons.

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