# d–d Spectral Assignments in Tetragonal Nickel(II) Complexes

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Cellular ligand field (CLF) analyses have been made for seven tetragonal-octahedral nickel(II) complexes $[NiCl_2(tfeh)_4]$ [tfeh = (tetrafluoroethyl)hydrazine] and $[NiX_2([n]aneN_4)]$ (X = $Cl^-$ or $NCS^-$; $n$ = 14, 15 or 16 and $[n]aneN_4$ represents an $n$-membered tetraaza macrocycle). Published assignments of the d–d spectra for all bar the $[14]aneN_4$ complexes lead to a π-acceptor function for $Cl^-$ and $NCS^-$. This result is chemically unreasonable for $Cl^-$ and previous studies indicate that $NCS^-$ is not a π acceptor towards $Ni^{II}$ either. The d–d spectra have been reinterpreted within the CLF framework leading to a consistent set of assignments and ligand-field parameters. The latter monitor the interplay between axial and equatorial bonding consistent with Pauling's electroneutrality principle: *i.e.* as the strength of the equatorial donation decreases [$e_\sigma$(N) gets smaller] the axial donors bind more strongly to compensate [$e_\sigma$(X) and $e_\pi$(X) increase] such that the sum, Σ, of all the CLF parameters remains essentially constant for the same donor sets. For the macrocyclic complexes the significant increases in the axial bonding parameters need not necessarily be accompanied by a marked decrease in the Ni–X bond length. Steric interactions between H atoms on the macrocyclic ring and the axial donors appear to prevent a closer approach.

Modern ligand-field analysis relies increasingly on the d–d spectra of transition-metal complexes.[1–7] The absorption spectrum can provide sufficient data to fix unique values for the ligand-field parameters, especially when the spectrum is correctly assigned. An assigned spectrum provides much more information than transition energies alone, often reducing ambiguity in the fitting process such that unique values for the ligand-field parameters can be derived. Ideally, assignments should be based on single-crystal measurements using polarised light. Single-crystal experiments are quite difficult, however, and relatively few such studies are reported.[8] Molecules are often unfavourably aligned while group theoretical selection rules may be ambiguous. This is especially so for centrosymmetric complexes where vibronic interactions and selection rules must be considered.[9]

Recourse is therefore usually made to unpolarised measurements often on a series of related complexes where empirical variations in the band energies can be correlated with changing donor sets. Such studies are normally guided by some form of crystal- or ligand-field theory. In the case of tetragonal nickel(II) complexes, which are the subject of this study, reproduction of the d–d band energies is relatively straightforward. By assuming $D_{4h}$ symmetry, such species have been treated by the 'traditional' crystal-field model employing the three global parameters $Dq$, $Ds$ and $Dt$.[10] However, while the transition energies can be reproduced, there is no guarantee of a reasonable description of the bonding since the global parameterisation cannot, in general, comment on the local nature of the metal–ligand interaction.[11]

Since the M–L bond describes a localised interaction, some form of local parameterisation is more appropriate. The cellular ligand field (CLF) model of Gerloch *et al.*[12] uses parameters which directly monitor the local σ and π interactions. The magnitudes and variations of the CLF $e_\lambda(\lambda = \sigma, \pi_x, \pi_y)$ parameters correlate with the structures and bonding in metal complexes and provide a more consistent way of comparing a series of species to determine whether the parameter values are reasonable. The CLF model provides not only an accurate method for reproducing experimental data but also a more detailed description of the nature of the M–L bond. The CLF scheme is therefore a more reliable approach for interpreting d–d spectra.

The advantages of the local CLF scheme over the global $Dq/Ds/Dt$ approach are illustrated in this paper by examining the spectra of seven tetragonal $NiN_4X_2$ complexes. The complexes $[NiCl_2(tfeh)_4]$[tfeh = (tetrafluoroethyl)hydrazine] and $[NiX_2([n]aneN_4)]$ (X = $Cl^-$ or $NCS^-$, $n$ = 14, 15 or 16 and $[n]aneN_4$ represents a fully saturated $n$-membered tetraaza macrocycle) are all characterised by four equatorial amine donors and two axial linear ligators. This leads to three CLF parameters $e_\sigma$(N), $e_\sigma$(X) and $e_\pi$(X), and hence, assuming $D_{4h}$ symmetry for illustrative purposes, to a direct mapping between the CLF and global schemes [equations (1)–(3)].[13] These

$$e_\sigma(\mathrm{N}) = (10/3)Dq \quad (1)$$

$$e_\sigma(\mathrm{X}) = (10/3)Dq - 2Ds - (5/2)Dt \quad (2)$$

$$e_\pi(\mathrm{X}) = -(3/2)Ds + (10/4)Dt \quad (3)$$

simple expressions already illustrate the potential problems of deriving local bonding information from a global scheme. While there is a direct relationship between the equatorial M–L interaction and $Dq$, the axial bonding is more complex and has contributions from all three global parameters. Thus, the relationships derived from variations in $Ds$ and $Dt$ with the nature of X may not correspond with the actual variation in σ and π bonding.

For example, the spectra of the macrocyclic complexes described above have been reproduced within the global scheme.[10] Converting the published values of $Dq$, $Ds$ and $Dt$ into the appropriate CLF values (see below) indicates π-donor roles for Cl and NCS in the $[14]aneN_4$ species but π-acceptor roles for the $[15]aneN_4$ and $[16]aneN_4$ molecules. Moreover, the published assignment for $[NiCl_2(tfeh)_4]$[14] yields a large *negative* $e_\pi$(Cl) of $-1750$ cm$^{-1}$ against an $e_\sigma$(Cl) of only 550 cm$^{-1}$. A π-acceptor role for $Cl^-$ is highly unlikely and, based on previous analyses of $[Ni(NH_3)_4(NCS)_2]$ and related molecules,[15] it appears that $NCS^-$ is also not a π-acceptor ligand at least towards $Ni^{II}$. The reason for these anomalies lies in the use of a global scheme which fails to make contact with the chemistry in these complexes. Consequently, the global

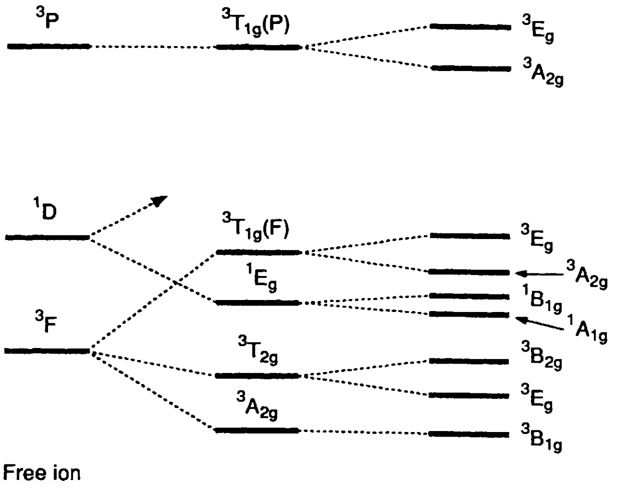

**Fig. 1** Qualitative partial energy-level scheme for tetragonal nickel(II) complexes. See text for detailed assignments for individual complexes

approach also leads to incorrect spectral assignments as will be seen.

These systems are therefore reanalysed within the CLF model. In contrast to the previous studies, the CLF model requires no artificial symmetry restrictions and $D_{4h}$ symmetry is *not* assumed. The actual reported structures derived from X-ray structural studies are employed. Spin-forbidden transitions are also included in the fitting process where appropriate, and use is made of published magnetic moments for [NiCl$_2$([15]aneN$_4$)].[10] Consistent sets of parameters emerge which require the spectra of five of the seven complexes to be reassigned. The resulting parameter values uncover an interesting feature of the nature of axial co-ordination to these macrocyclic systems in that an increase in donor strength need not be accompanied by a decrease in bond length.

## Ligand-field Analyses

The CLF model is not restricted to any idealised symmetry. The present analyses therefore used the reported structures derived from X-ray crystallography.[14,16] All calculations employed the three CLF parameters, $e_\sigma$(N), $e_\sigma$(X) and $e_\pi$(X) (X = Cl or NCS) representing the equatorial σ, axial σ and axial π interactions respectively. The Ni–NCS angles are 165.1, 153.8 and 160° for the [14]-, [15]- and [16]-aneN$_4$ isothiocyanate complexes respectively.[16] A Ni–NCS angle of 140° in [Ni(en)$_2$(NCS)$_2$] (en = ethane-1,2-diamine) was associated with a degree of misdirected valence.[15] However, the results of the present analysis indicate that such interactions are not resolvable here (see below) and the NCS ligand was treated as a linear ligator. All calculations save those for the [14]aneN$_4$ complexes employed the full d$^8$ basis comprising $^3$F, $^3$P, $^1$S, $^1$D and $^1$G terms. The [14]aneN$_4$ species do not exhibit any spin-forbidden transitions and therefore only require a $^3$F, $^3$P basis set. In addition, the calculations employed the Condon–Shortley interelectron repulsion parameters $F_2$ and $F_4$ for the full-basis calculations or just the Racah $B$ parameters for the spin-triplet calculations. A nominal value of 500 cm$^{-1}$ was taken for the spin–orbit coupling constant, ζ, except for [NiCl$_2$([15]aneN$_4$)] where the value was optimised against the observed magnetic moment.

All the complexes have approximately $D_{4h}$ symmetry and the energy levels are labelled accordingly as in Fig. 1. The ground state is of $^3B_{1g}$ symmetry with excited triplet states of $^3E_g$ and $^3B_{2g}$, derived from the parent octahedral $^3T_{2g}$ term, and two sets of $^3A_{2g}$ and $^3E_g$ levels derived from the parent octahedral $^3T_{1g}$(F) and $^3T_{1g}$(P) terms. The only singlet levels of relevance here are the $^1A_{1g}$ and $^1B_{1g}$ levels derived from the octahedral $^1E_g$ term. The transition $^3B_{1g} \longrightarrow {}^3B_{2g}$ depends solely on $e_\sigma$(N). Note, however, that this energy is rigorously equal to 3$e_\sigma$(N) *only* when the in-plane bond angles are exactly 90°.

[NiCl$_2$(tfeh)$_4$].—The structure and d–d band maxima for [NiCl$_2$(tfeh)$_4$] have been reported by Rahman *et al.*[14] Band energies are given as 8700, 10 600, 12 900, 17 400 and 27 400 cm$^{-1}$ assigned as transitions to $^3E_g$, $^3B_{2g}$, $^3A_{2g}$, $^3E_g$ and the unsplit components of the (octahedral) $^3T_{1g}$(P) term respectively. Reproduction of these energies to within a few hundred wavenumbers yields CLF parameter values of 3533, 550 and −1750 cm$^{-1}$ for $e_\sigma$(N), $e_\sigma$(Cl) and $e_\pi$(Cl) respectively. Clearly, such a large negative $e_\pi$(Cl) value suggests a chemically unacceptable π-acceptor role for Cl$^-$ and indicates that the published assignment needs revision. Given that the band at 27 400 cm$^{-1}$ corresponds to unsplit $^3A_{2g}$ and $^3E_g$ levels derived from the octahedral $^3T_{1g}$(P) term, it follows that the $^3T_{1g}$(F) term should also remain essentially unsplit.[9] If the transition to the $^3A_{2g}$ level, originally placed at 12 900 cm$^{-1}$, is reassigned to lie under the band at 17 400 cm$^{-1}$, then one of the first three bands must correspond to a spin-forbidden process while the other two correspond to the transitions to $^3E_g$ and $^3B_{2g}$. The latter is determined by $e_\sigma$(N) which would take values of 2900, 3533 and 4300 cm$^{-1}$ respectively.

Previous studies[13,17] indicate a good correlation between bond length and $e_\sigma$ for saturated equatorial nitrogens in tetragonal nickel systems. The Ni–N bond length in [NiCl$_2$(tfeh)$_4$] of 2.106 Å suggests a value for $e_\sigma$(N) of 4300 cm$^{-1}$ is most likely and therefore the band at 12 900 cm$^{-1}$ is reassigned as the $^3B_{1g} \longrightarrow {}^3B_{2g}$ transition. The most likely assignment of the spin-forbidden process is to the band at 10 600 cm$^{-1}$ which then yields the best-fit CLF parameter values given in Table 1. The observed and calculated transition energies are compared in Table 2. The choice of assignment is further supported by the satisfactory reproduction of the experimental spectrum by CLF parameter values which are more consistent with previous studies and this work (see below).

[NiCl$_2$([14]aneN$_4$)].—Six bands are reported[10] for [NiCl$_2$([14]aneN$_4$)] and assigned to spin-allowed transitions as per Fig. 1. Reproduction of these band energies gives the essentially unique CLF parameter values displayed in Table 1. The agreement with experiment (Table 2) is again satisfactory while the CLF parameter values appear unexceptional. There is no case to be made for reassigning the spectrum based on the ligand-field analysis.

[NiCl$_2$([15]aneN$_4$)].—Martin *et al.*[10] also report six absorption maxima for [NiCl$_2$([15]aneN$_4$)], again assigned as per Fig. 1. However, the CLF analysis based on this assignment leads to $e_\sigma$(N) = 4152, $e_\sigma$(Cl) = 1680 and $e_\pi$(Cl) = −180 cm$^{-1}$. As found for [NiCl$_2$(tfeh)$_4$], the Cl ligand is predicted to be a π acceptor and again indicates a questionable assignment. Further complications arise in that the spectrum actually displays three bands in the 12 000–13 000 cm$^{-1}$ region, only one of which was assigned to a spin-allowed transition while the other, presumably spin-forbidden, bands were ignored. The present CLF analysis therefore seeks not only to derive a more consistent set of parameter values but also to account for the spin-forbidden features. The original paper does not report all the band maxima. Approximate values of 11 900, 12 750 and 13 100 cm$^{-1}$ were derived graphically from Fig. 6 of ref. 10.

Three assignments were examined in which the $^3B_{2g}$ level is associated with the bands at 13 100, 12 750 and 11 900 cm$^{-1}$ respectively. Fixing the $^3B_{2g}$ energy immediately determines the value of $e_\sigma$(N) while the $^1B_{1g}$ to $^1A_{1g}$ splitting depends on $e_\sigma$(Cl) and ζ. A lower limit in ζ can be evaluated by computing the effective magnetic moment assuming that Steven's orbital-

**Table 1** Best-fit CLF and interelectron repulsion parameter values (cm$^{-1}$), metal–ligand bond lengths (Å) and CLF sum values (cm$^{-1}$) for tetragonal $NiN_4X_2$ complexes

| Complex | $e_\sigma$(N) | Ni–N | $e_\sigma$(X) | Ni–X | $e_\pi$(X) | $B/F_2$[a] | $F_4$ | Σ |
|---|---|---|---|---|---|---|---|---|
| $[NiCl_2(tfeh)_4]$ | 4 300 | 2.106 | 2 480 | 2.444 | 400 | 1 196 | 68 | 23 760 |
| $[NiCl_2([14]aneN_4)]$ | 4 976 | 2.067 | 1 580 | 2.510 | 240 | 790[b] | — | 24 024 |
| $[NiCl_2([15]aneN_4)]$ | 4 390 | 2.144 | 2 250 | 2.497 | 575 | 1 328 | 106 | 24 360 |
| $[NiCl_2([16]aneN_4)]$ | 3 779 | 2.171 | 3 100 | 2.482 | 900 | 1 356 | 106 | 24 916 |
| $[Ni(NCS)_2([14]aneN_4)]$ | 4 780 | 2.067 | 3 000 | 2.130 | 100 | 790[b] | — | 25 720 |
| $[Ni(NCS)_2([15]aneN_4)]$ | 4 072 | 2.131 | 3 600 | 2.079 | 500 | 1 300 | 93 | 25 488 |
| $[Ni(NCS)_2([16]aneN_4)]$ | 3 632 | 2.179 | 4 100 | 2.077 | 750 | 1 278 | 87 | 25 728 |

[a] $F_2$ if value for $F_4$ given, otherwise $B$. [b] Estimated value.

**Table 2** Observed and calculated d–d transition energies for tetragonal $NiN_4X_2$ species. Calculated spectra use best-fit parameter values from Table 1

| Complex | $^3B_{1g} \longrightarrow$ | $^3B_{2g}$ | $^3E_g$ | $^1A_{1g}$, $^1B_{1g}$ | $^3A_{2g}$(F), $^3E_g$(F) | $^3A_{2g}$(P), $^3E_g$(P) |
|---|---|---|---|---|---|---|
| $[NiCl_2(tfeh)_4]$ | obs.[a] | 12 900 | 8 700 | 10 600 | 17 400 | 27 400 |
| | calc. | 12 935 | 8 936, 9 299 | 10 146, 11 209 | 15 890, 17 609, 17 816 | 26 967, 28 077, 28 188 |
| $[NiCl_2([14]aneN_4)]$ | obs. | 14 750[b] | 8 600 | — | 15 200,[b] 19 400 | 27 100, 29 300 |
| | calc. | 14 748 | 8 457, 8 885 | — | 15 156, 18 488, 19 864 | 26 808, 28 005, 29 253 |
| $[NiCl_2([15]aneN_4)]$ | obs.[a] | 13 100[b] | 8 664 | 11 900,[b] 12 750[b] | 14 421, 17 602 | 26 100, 27 299 |
| | calc. | 13 120 | 8 736, 8 283 | 11 895, 12 756 | 15 186, 16 963, 17 745 | 25 522, 26 814, 27 534 |
| $[NiCl_2([16]aneN_4)]$ | obs.[a] | 11 157 | 7 782 | 13 455 | 15 758 | 25 621 |
| | calc. | 11 154 | 8 079, 8 510 | 13 422 | 14 217, 15 054, 15 604 | 24 792, 25 490, 25 688 |
| $[Ni(NCS)_2([14]aneN_4)]$ | obs. | 14 150[b] | 11 080 | — | 17 800, 20 225 | — |
| | calc. | 14 156 | 11 083, 11 427 | — | 17 772, 19 301, 20 541 | 29 396, 29 690, 30 814 |
| $[Ni(NCS)_2([15]aneN_4)]$ | obs.[a] | 12 029[b] | 10 326 | 12 900 | 15 834,[b] 18 367 | 28 514 |
| | calc. | 12 007 | 10 281, 10 535 | 12 825, 13 000 | 17 057, 17 588, 17 867 | 27 736, 28 081, 28 384 |
| $[Ni(NCS)_2([16]aneN_4)]$ | obs.[a] | 10 724[b] | 9 606[b] | 12 500[b] | 16 500 | 27 063 |
| | calc. | 10 784 | 9 950, 10 090 | 12 445, 12 480 | 16 049, 16 491, 16 940 | 27 031, 27 135, 27 290 |

[a] Spectrum reassigned. [b] Estimated peak energy (usually by Gaussian analysis).

reduction parameter, $k$, must be less than or equal to unity. The upper limit on $\zeta$ is presumably the free-ion value of 650 cm$^{-1}$.[18] For $k = 1$ a $\zeta$ value of about 600 cm$^{-1}$ gives a calculated $\mu_{eff}$ of 3.220 *versus* the experimental value of 3.22, while for $\zeta = 650$ cm$^{-1}$, $k$ is required to be about 0.94 in order to reproduce $\mu_{eff}$. Best-fit CLF parameter values $e_\sigma$(N), $e_\sigma$(Cl) and $e_\pi$(Cl) for each assignment, and with $\zeta = 600$ cm$^{-1}$, are as follows: $^3B_{2g}$ at 13 100 gives 4390, 2250 and 575 cm$^{-1}$; $^3B_{2g}$ at 12 700 gives 4265, 2850 and 950 cm$^{-1}$; $^3B_{2g}$ at 11 900 cm$^{-1}$ gives 3985, 3200 and 1100 cm$^{-1}$. The biggest difference between these fits is that the last two assignments predict much larger Cl parameter values than those of the first. Given the values for $e_\sigma$(Cl) and $e_\pi$(Cl) of 2480 and 400 cm$^{-1}$ for $[NiCl_2(tfeh)_4]$, it is tempting to conclude that the values for the last two assignments for the $[14]aneN_4$ species are in fact too large. The values for the first assignment appear to be most reasonable and these data are reported in Table 1 with the computed transition energies in Table 2. Further justification for this choice of CLF parameter values is given below.

$[NiCl_2([16]aneN_4)]$.—Only five bands are reported[10] for $[NiCl_2([16]aneN_4)]$, the splitting of the levels derived from the $^3P$ term apparently being unresolved. Again, fitting this assignment within the CLF scheme leads to a negative $e_\pi$(Cl) value of $-200$ cm$^{-1}$. However, the observation that the parent $^3P$ term does not split parallels the $[NiCl_2(tfeh)_4]$ case. Reassigning the spectrum of $[NiCl_2([16]aneN_4)]$ in like fashion leads to two bands being placed under the absorption at 15 758 cm$^{-1}$ while the peak at 13 455 cm$^{-1}$ is treated as a spin-forbidden transition. This yields the best-fit CLF parameter values shown in Table 1 with the calculated spectrum given in Table 2.

$[Ni(NCS)_2([14]aneN_4)]$.—Four d–d peak energies are reported[10] for $[Ni(NCS)_2([14]aneN_4)]$. Evidently transitions to levels derived from the $^3P$ free-ion term are not observed so only nominal values for the interelectron repulsion parameters can be used. The spectrum is assigned as per Fig. 1. Reproducing these transitions by CLF calculations yields the parameter values and calculated band energies given in Tables 1 and 2 respectively. As found for the dichloro complex, a reassignment of the spectrum is not warranted nor are any spin-forbidden transitions observed.

$[Ni(NCS)_2([15]aneN_4)]$.—Five band maxima are given[10] for $[Ni(NCS)_2([15]aneN_4)]$ although the features at 12 029 and 15 834 cm$^{-1}$ were derived by Gaussian analysis. As for the analogous chloro species, reproduction of the reported assignment within the CLF scheme indicates a $\pi$-acceptor role for NCS. The parameter values are 4072, 2250 and $-600$ cm$^{-1}$ for $e_\sigma$(N), $e_\sigma$(NCS) and $e_\pi$(NCS) respectively. The isothiocyanate values are inconsistent with those derived for $[Ni(NCS)_2([14]aneN_4)]$. The Ni–NCS bond length decreases in $[Ni(NCS)_2([15]aneN_4)]$ from 2.130 to 2.079 Å yet the $e_\pi$(NCS) value for the latter decreases. Moreover, NCS is a $\pi$ donor in the $[14]aneN_4$ species but apparently a $\pi$ acceptor in the $[15]aneN_4$ complex. Both observations suggest that the spectrum should be reassigned.

Closer inspection of the experimental spectral plot[10] indicates that the broad absorption between 12 000 and 13 000 cm$^{-1}$ may contain more than the $^3B_{1g} \longrightarrow {}^3B_{2g}$ transition at 12 029 cm$^{-1}$. Indeed, weak absorption around 12 900 cm$^{-1}$ is suggested and assigned to spin-forbidden processes. Moreover, given the general uncertainty inherent in the Gaussian analysis procedure, the exact energy of the $^3B_{1g} \longrightarrow {}^3A_{2g}$ band, reported at 15 834 cm$^{-1}$, is uncertain. Accordingly, both components of the transition to the nominal (octahedral) $^3T_{1g}$(F) term are placed under the absorption at 18 367 cm$^{-1}$. This assignment correlates with the observation of only a single band for the transitions to the $^3T_{1g}$(P) levels and with the proposed reassignments for $[NiCl_2(tfeh)_4]$ and $[Ni(NCS)_2([16]aneN_4)]$. Reproduction of the reassigned spectrum yields the parameter values and transition energies reported in Tables 1 and 2 respectively.

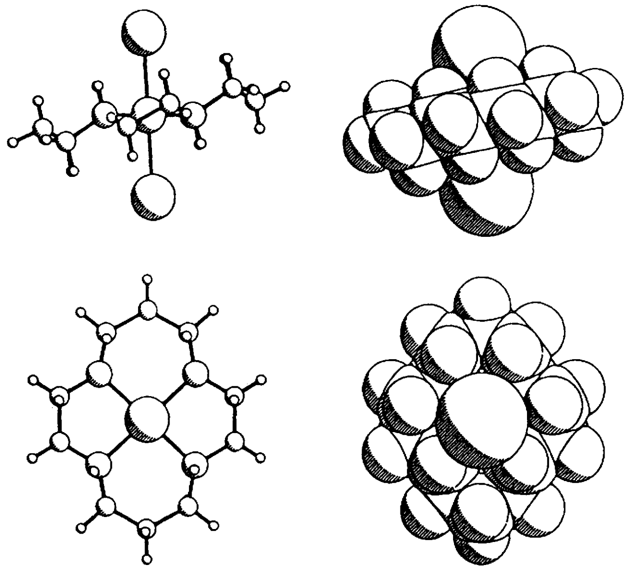

**Fig. 2** Molecular and space-filling representations of [NiCl$_2$-([14]aneN$_4$)] derived from X-ray structural data (ref. 16)

[Ni(NCS)$_2$([16]aneN$_4$)].—The CLF analysis of [Ni(NCS)$_2$-([16]aneN$_4$)] is qualitatively the same as for the [15]aneN$_4$ analogue save that the extra low-energy spin-forbidden band is better resolved. The reported assignment leads to unreasonable isothiocyanate parameters [$e_\sigma$(NCS) = 2600, $e_\pi$(NCS) = $-300$ cm$^{-1}$] while a reassignment analogous to that for [Ni-(NCS)$_2$([15]aneN$_4$)] gives more reasonable parameter values (Table 1) with acceptable reproduction of the experimental band energies (Table 2).

## Discussion

The CLF analyses suggest that for the tetragonal nickel(II) complexes studied here five d–d spectra out of seven require reassignment. The basis for these decisions is the reasonableness or otherwise of the CLF parameter values which in turn rests on the connection between the CLF parameters and the nature of the metal–ligand bonding. There is no doubt that the CLF scheme reproduces the experimental data as well or better than any other ligand-field approach[19] but it is the detailed commentary provided by the $e_\lambda$ parameters on the local electron distributions and bonding which makes the CLF model a more powerful and useful tool. This assertion has been borne out on many occasions.[1–7] The CLF model provides a consistent description of the electronic structures and metal–ligand interactions for a wide variety of transition-metal complexes. Some of this work is especially relevant here since it supports the choice of $e_\lambda$ values given in Table 1.

Many authors have analysed the spectra of tetragonal nickel(II) amine species.[10,13,15,17] Although descriptions of the axial ligands have, in the light of more sophisticated CLF treatments, required revision,[15] a general conclusion to emerge from all the studies is the essentially linear correlation between $e_\sigma$(N) and the equatorial Ni–N bond length over the range 2.0–2.3 Å.[13,16,17] The value of $e_\sigma$(N) is determined by the $^3B_{1g} \longrightarrow {}^3B_{2g}$ energy which was apparently correctly assigned for all the macrocyclic species. This is not surprising since for $D_{4h}$ Ni$^{II}$ the $^3B_{1g} \longrightarrow {}^3B_{2g}$ splitting is equal to 10*Dq* so that even in the global *Dq*/*Ds*/*Dt* scheme the increase in the Ni–N bond length with increasing ring size is expected to correlate with a decreasing value for 10*Dq*. Hence, for saturated equatorial nitrogen donors, an obvious trend is expected even for the global parameterisation scheme.

Where the global scheme breaks down is in the treatment of the axial donors. Such an approach fails to show that for the [15]- and [16]-aneN$_4$ complexes the apparently most obvious assignment of the d–d spectra leads to chemically unreasonable bonding parameters. In the CLF model, however, more is demanded than simply reproducing the band energies. The parameter values must also make chemical sense. The theoretical justification of the chemical relevance of $e_\lambda$ parameters has been described in detail before.[12] Suffice it to say here that, other things being equal, chloride is not expected to behave as a $\pi$ acceptor under *any* circumstances. Moreover, previous CLF analyses of [Ni(NH$_3$)$_4$(NCS)$_2$], [Ni(en)$_2$(NCS)$_2$] and Ni(tmen)$_2$(NCS)$_2$] (tmen = *N,N,N′,N′*-tetramethylethane-1,2-diamine) also suggest[15] that linearly co-ordinated isothiocyanate is not a $\pi$ acceptor towards Ni$^{II}$ either. The $e_\pi$ parameters for the present systems should always be positive.

An interesting feature of the data in Table 1 is the inverse correlation between equatorial and axial parameter values. As $e_\sigma$(N) decreases, $e_\sigma$(X) and $e_\pi$(X) increase. This is an obvious example of Pauling's electroneutrality principle: as the donation from the equatorial ligands decreases, the axial ligands donate more strongly to compensate. Similar behaviour has been observed in other tetragonal nickel(II) amine systems.[15] Within the CLF model, Pauling's electroneutrality principle seems to have another important consequence. That is, in a series of related complexes, the sum of all the diagonal CLF parameter values, $\Sigma$, is approximately constant. This result has been observed empirically[1] and rationalised theoretically.[20] The so-called CLF sum rule has since been applied successfully to probe the nature of the bonding in chlorocuprates(II)[2] and represents a powerful method for reducing the degree of ambiguity in ligand-field analysis. The $\Sigma$ values for the present complexes are also listed in Table 1. For the chloro species, $\Sigma = 24\,300 \pm 600$ cm$^{-1}$ while for the isothiocyanato complexes $\Sigma = 25\,600 \pm 130$ cm$^{-1}$. The latter compares well with values from previous studies[15] on other Ni–NCS complexes.

The present analyses also highlight the essential difference between the CLF model and the earlier molecular orbital (MO)-based angular overlap model (AOM).[21] In the AOM the value of $e_\lambda$ is proportional to the square of the appropriate diatomic overlap integral. However, the relationship has been shown empirically to be unreliable while it is theoretically invalid within the CLF formalism.[1] In the present case, for example, the AOM would predict essentially identical chloride parameter values for all three macrocyclic complexes since the Ni–Cl distances are essentially the same. The CLF model does not suffer from this restriction and predicts that the axial Cl ligands donate more strongly without shortening the bond length significantly. Similar behaviour is well known in copper(II) complexes. For example, trigonal-bipyramidal species like [Cu(bipy)$_2$X] (bipy = 2,2′-bipyridine, X = I or NH$_3$) have bipyridyl ligands spanning axial and equatorial sites with very similar Cu–N distances, yet the axial $e_\sigma$ parameter is about twice as large as the equatorial value.[3] This result correlates nicely with the stereochemical activity of the incomplete d shell.[22]

In the macrocyclic nickel complexes steric interactions presumably prevent the closer approach of Cl. Fig. 2 displays space-filling representations for [NiCl$_2$([14]aneN$_4$)] which indicate that the H atoms, especially those connected to the ring nitrogens, come into fairly close contact with the axial ligands. However, the demands of electroneutrality still oblige the latter to donate more strongly as the equatorial donation weakens. In contrast, the smaller NCS ligand is able to approach more closely if required. Hence, for [Ni(NCS)$_2$([14]aneN$_4$)], where the equatorial Ni–N interaction is strong and the bond length the shortest, the axial NCS donation is relatively weak and the Ni–NCS bond length is 2.130 Å. For the [15]aneN$_4$ complex the equatorial donation weakens significantly and the axial bonding strengthens to compensate. Here the enhanced axial binding is accompanied by a shortening of the Ni–NCS bond from 2.130 to 2.079 Å. Thereafter, in the [16]aneN$_4$ complex, the steric interaction between the macrocycle and the NCS ligands prevents any further contraction of the N–NCS contact, which remains essentially unchanged at 2.077 Å. Nevertheless, electroneutrality requires the NCS ligands in [Ni(NCS)$_2$-([16]aneN$_4$)] to donate more strongly as monitored by an increase in the NCS CLF parameter values.

## Conclusion

The CLF model applied to seven tetragonal nickel(II) complexes has demonstrated that the assignments of several of the d–d spectra lead to chemically unreasonable CLF parameter values. These spectra were originally analysed using a global parameterisation of the ligand field. This work indicates that such schemes can give erroneous results and are therefore of limited value for interpreting the spectra of low-symmetry species.

The spectra were therefore reanalysed within the CLF formalism. A self-consistent and chemically useful description of the metal–ligand bonding in these systems emerges. In particular, the demands of the electroneutrality principle are evident in that as the strength of the equatorial bonding decreases the axial ligands donate more strongly. Thus, as the equatorial CLF parameter value falls the axial parameters increase. This interplay is monitored by the CLF sum, Σ, which, for a given set of donor atoms (*i.e.* $N_4Cl_2$ or $N_4N'_2$), remains essentially constant.

Interestingly, the significant *increase* in axial interaction in the series [14]-, [15]- to [16]-aneN$_4$ need not necessarily be accompanied by a similarly dramatic *decrease* in the axial bond length. In the macrocyclic complexes steric interactions appear to hold the relatively large $Cl^-$ ligands at more or less the same distance for all three ring sizes. In contrast, the smaller nitrogen donor atom of the $NCS^-$ ligand initially allows for a shortening of the bond from the [14]- to the [15]-aneN$_4$ species. Thereafter, the $NCS^-$ too is held at the same distance for the [16]aneN$_4$ complex, even though the ring size has increased.

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## References

1 R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1984, **23**, 3846.
2 R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1984, **23**, 3853.
3 R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1985, **23**, 1754.
4 C. A. Brown, M. J. Duer, M. Gerloch and R. F. McMeeking, *Mol. Phys.*, 1988, **64**, 793.
5 N. D. Fenton and M. Gerloch, *Inorg. Chem.*, 1989, **28**, 2767.
6 M. J. Duer and M. Gerloch, *J. Chem. Soc., Dalton Trans.*, 1989, 2109.
7 M. J. Duer and M. Gerloch, *Inorg. Chem.*, 1989, **28**, 4260.
8 M. A. Hitchman, *Transition Met. Chem. (New York)*, 1985, **9**, 1.
9 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier, Amsterdam, 1984.
10 L. Y. Martin, C. R. Sperati and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 2968.
11 M. Gerloch, *Magnetism and Ligand Field Analysis*, Cambridge University Press, 1984.
12 M. Gerloch, J. H. Harding and R. G. Woolley, *Struct. Bonding (Berlin)*, 1981, **46**, 1.
13 I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, 1976, **15**, 2014.
14 A. A. Rahman, M. P. Brown, M. M. Harding, C. E. Keggan and J. D. Nicholls, *Polyhedron*, 1988, **7**, 1147.
15 R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1987, **26**, 2582.
16 T. Ito, M. Kato and H. Ito, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2641.
17 A. B. P. Lever, I. M. Walker, P. J. McCarthy, K. B. Mertes, A. Jircitano and R. Sheldon, *Inorg. Chem.*, 1983, **22**, 2252.
18 J. S. Griffith, *The Theory of Transition-Metal Ions*, Cambridge University Press, 1961.
19 M. Gerloch and R. G. Woolley, *Prog. Inorg. Chem.*, 1983, **31**, 371.
20 R. G. Woolley, *Chem. Phys. Lett.*, 1985, **118**, 207.
22 C. K. Jorgensen, *Struct. Bonding (Berlin)*, 1964, **1**, 3.
22 R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1985, **24**, 4490.

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