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THE ELECTRONIC SPECTRA OF TETRAGONAL METAL COMPLEXES ANALYSIS AND SIGNIFICANCE

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Whilst many physical techniques play their part in the elucidation of the geometric and electronic structure of a metal complex, a study of the electronic spectra can often provide the most detailed information. In the spectrum we see a map of the energy levels within the molecule—the trick is to learn how to read this map.

There are perhaps two primary stages in this map reading—assignment of the observed bands to specific transitions within the molecule, and calculation of the transition energies in terms of a given set of parameters. The assignments depend upon, amongst other things, the stereochemistry of the molecule—thus band assignments necessarily lead to some knowledge about the stereochemistry of the complex.

The energy parameters depend upon the chemical bonding within the molecule and therefore can provide information about the bonding. In cubic molecules the parameters generally employed are *Dq*, the crystal field splitting parameter and B (and perhaps C) the Racah inter-electronic repulsion parameter. The variation of these with respect to the metal or ligand gives rise to the well known spectrochemical and nephelauxetic series.

These parameters can provide information about the degree of σ and/or π bonding in the metal ligand bond, about the effective charge on the metal and the mean d orbital radius.

Most of the analytical work in this area has been carried out with cubic molecules ML_n, so that we obtain information about the ML bond in the presence of other ML bonds. Of potentially greater interest is to be able to study the ML bond in the presence of other MX bonds. For example in the molecule ML_pX_q, how is the ML bond affected by the presence of the X ligands, and how is the MX bond affected by the presence of the L ligands? We could use the X ligand as a probe to study the ML bond, and *vice versa*.

This paper will describe the methods which are being employed to investigate this sort of problem, with especial relevance to tetragonal molecules of microsymmetry ML_4Z_2. First, however, it is necessary to consider how the spectra of such molecules differ from their cubic analogues. The discussion is restricted to the first row transition series, since it is here that most work has been carried out.

Cubic molecules may be divided into three basic groups:
i) central ions with free ion ground states of total orbital angular momentum 3, *i.e.* F states
ii) central ions with free ion ground states of total angular momentum 0, *i.e.* S states and iii) central ions with free ion ground states of total angular momentum 2, *i.e.* D states. It is convenient to divide the discussion of tetragonal molecules into these three categories.

The first category may be further sub-divided according to whether the ground state in an octahedral environment is A_{2g} or T_{1g}. We shall be concerned with examples of the first type, (orbital singlet ground state) where a great deal of information is available. Few tetragonal complexes of ions with octahedral T_{1g} ground states have been characterised.

Ions belonging to the second category (ii) above, whose octahedral ground states is A_{1g}, might usefully be included in a general discussion of A_{2g} octahedral ground state ions. Thus the following discussion will refer generally to tetragonal complexes of d^3 and d^8 ions (primarily chromium(III) and nickel(II) and spin-paired d^6 ions (cobalt(III)). Octahedral complexes of d^3 and d^8 ions give rise to a spectrum consisting of three spin-allowed transitions from the A_{2g} ground state to the T_{2g}, T_{1g} (F) and T_{1g}(P) levels. In a similar manner, spin-paired d^6 systems yield two fairly low energy spin-allowed transitions from A_{1g} to T_{1g} and T_{2g}.

In descending in symmetry to D_{4h}, the ground state of course remains an orbital singlet, but all the excited states noted above will split into two levels, an orbital singlet plus an orbital doublet (E_g). In descending to D_{4h} symmetry, the octahedral levels of d^3, d^8 and spin-paired d^6 molecules, transform as follows:

d^3, d^8

$$\begin{array}{cccc} A_{2g} & T_{2g} & T_{1g} & T_{1g}(P) \\ \downarrow & \downarrow \quad \downarrow & \downarrow \quad \downarrow & \downarrow \quad \downarrow \\ B_{1g} & B_{2g}+E_g & A_{2g}+E_g & A_{2g}(P)+E_g(P) \end{array}$$

d^6

$$\begin{array}{ccc} A_{1g} & T_{1g} & T_{2g} \\ \downarrow & \downarrow \quad \downarrow & \downarrow \quad \downarrow \\ A_{1g} & A_{2g}+E_g & B_{2g}+E_g \end{array}$$

Thus, in theory our three band spectrum becomes a six band spectrum and should therefore contain enough information to analyse satisfactorily. In practice all six bands are rarely seen. It is generally true that the lowest energy spin-allowed transition is most susceptible to the effects of lower symmetry. Molecules of the general class ML_4Z_2 belonging to this group, frequently exhibit a solution spectrum in which the first 'octahedral' band is split into two well defined components. It is also generally true, that the higher energy spin-allowed transitions remain unsplit, *i.e.* as far as these bands are concerned the molecule appears to be octahedral. This does not necessarily imply that the higher orbital triplet states are not split by the lower symmetry field. Transitions observed in solution or in the solid state at room temperature are generally rather broad, for a number of reasons, principally because they contain a number of component vibrational transitions. For this reason if the splitting of an excited state is less than about 1500 cm^{-1} transitions to these levels are not likely to be resolved. They may however show up if low temperature studies are carried out. In practice it appears that the splitting of the 1st excited state is nearly always greater than the splitting of higher excited states. Some examples of the spectra of tetragonal chromium(III), nickel(II), and cobalt(III) complexes are given in figures 1–3.

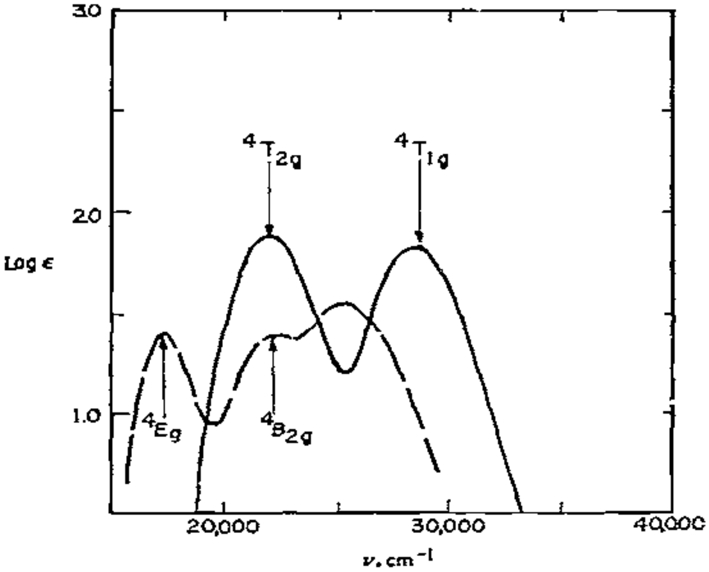
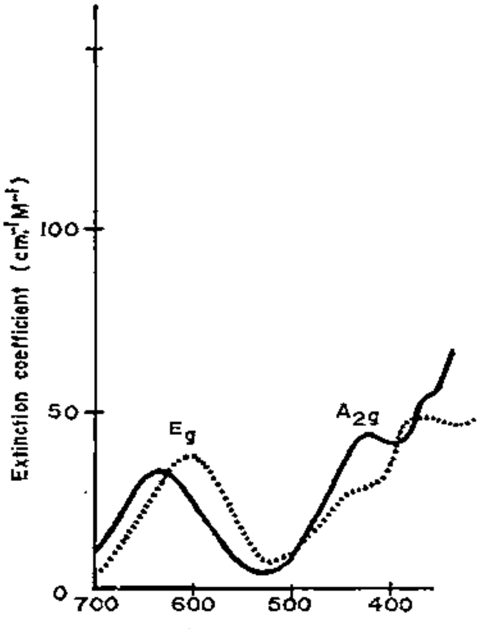


Fig. 1. Spectra of Cren$_3^{3+}$ (———) and *trans*-Cren$_2$Cl$_2^+$ (– – –) [Adapted from ref. 17].

There are several possible approaches to the analysis of spectra of this type, *viz.* i) to utilise the crystal field approach and assume that the tetragonal field is a perturbation on the cubic (octahedral) environment, ii) to utilise one of several molecular orbital approaches which characterise the energy levels in terms of the differences between the σ and π bonding capabilities of the ligands concerned, or (iii) to use a strong field approach in which the tetragonal nature of the molecule is recognised as of prime importance. The high spin energy levels of cubic molecules may be described, in crystal field theory, by means of the interelectronic repulsion parameter B and by one crystal field radial integral *Dq*. Two further crystal field parameters, *Ds* and *Dt*, are needed to describe the energy levels of tetragonal molecules.

Ds is a second order radial integral, which has no counterpart in cubic molecules, whilst *Dt* is fourth order, and as will be seen below, is related to the parameter *Dq*.



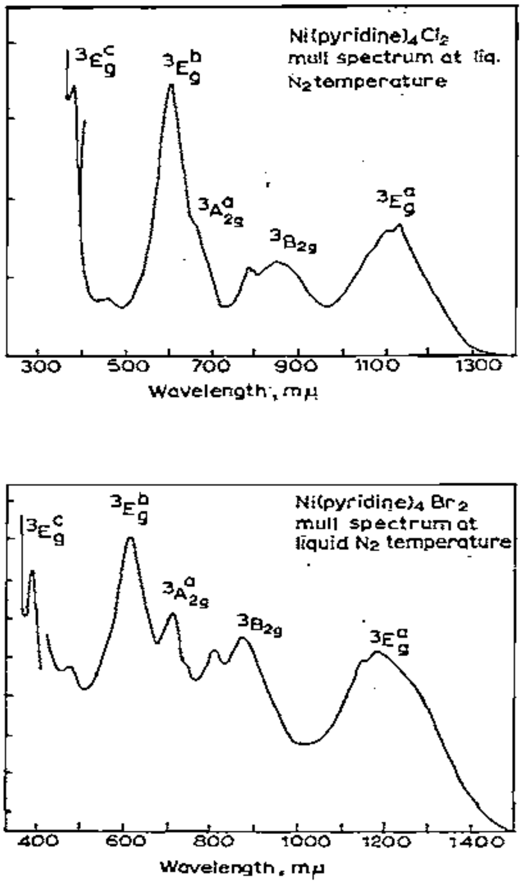


Fig. 2. Electronic spectra of *trans*- (Coen$_2$Cl$_2$)$^+$Cl$^-$(····) and trans-(Cocyclam Cl$_2$)$^+$Cl$^-$(——) showing the splitting of the T_{1g} level into $E_g + A_{2g}$.

Fig. 3. Electronic transmittance spectra at liquid N$_2$ temperature (Nujol Mull)[15] of NiPy$_4$Cl$_2$ and NiPy$_4$Br$_2$.
(Adapted from D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 6 (1967) 1092).

$$Ds = \int [R_{3d}(r)]^2 3/2f_2(r)d\tau$$
$$Dt = \int [R_{3d}(r)]^2 3/2f'_4(r)d\tau$$

The transition energies, neglecting for the moment, configurational interaction between levels of the same symmetry, are given in Table I.

Four pieces of independent spectroscopic information will be required in order to make a complete analysis of the spectrum. In general insufficient information is available. The splitting of the first band provides two pieces of data. If the remaining bands do not exhibit splitting, it is possible to make the assumption that, for example, the A$_2$ and E components of the T_{1g} level are equal to each other and to the observed band energy. In this way it would be possible to solve the

TABLE 1

TRANSITION ENERGIES IN TETRAGONAL MOLECULES *trans*-ML_4Z_2; CRYSTAL FIELD APPROXIMATION

d^6 *Complexes*		
$^1A_{2g} \leftarrow {}^1A_{1g}$	$10Dq_L - C$	Splitting of $^1T_{1g}$
$^1E_g{}^a \leftarrow {}^1A_{1g}$	$10Dq_L - 35/4\ Dt - C$	$+35/4\ Dt$
$^1B_{2g} \leftarrow {}^1A_{1g}$	$10Dq_L - 4Ds - 5Dt + 16B - C$	Splitting of $^1T_{2g}$
$^1E_g{}^b \leftarrow {}^1A_{1g}$	$10Dq_L + 2Ds - 25/4\ Dt + 16B - C$	$-6Ds + 5/4\ Dt$
d^3,d^8 *Complexes*		
$B_{2g} \leftarrow B_{1g}$	$10Dq_L$	Splitting of T_{2g}
$E_g{}^a \leftarrow B_{1g}$	$10Dq_L - 35/4\ Dt$	$+35/4\ Dt$
$A_{2g}{}^a \leftarrow B_{1g}$	$R(-) - 4Ds + 2Dt$	Splitting of T_{1g}(F)
$E_g{}^b \leftarrow B_{1g}$	$R(-) + 2Ds + 3/4\ Dt$	$-6Ds + 5/4\ Dt$
$A_{2g}{}^b \leftarrow B_{1g}$	$R(+) + 2Ds - 8Dt$	Splitting of T_{1g}(P)
$E_g{}^c \leftarrow B_{1g}$	$R(+) - Ds - 3Dt$	$3Ds - 5Dt$
$R(-) = \frac{1}{2}[15B + 30Dq_L - (225B^2 + 100Dq_L{}^2 - 180BDq_L)^{\frac{1}{2}}]$ $R(+) = \frac{1}{2}[15B + 30Dq_L + (225B^2 + 100Dq_L{}^2 - 180BDq_L)^{\frac{1}{2}}]$		$10Dq_L \equiv Dq_{xy}$

spectrum; however the error introduced by such an assumption may be considerable since the A_2 and E components could in reality differ by as much as 1500 cm^{-1}—this procedure is therefore not recommended.

In the absence of the necessary pieces of information, is it possible to make some useful deductions from the observed spectrum? Many authors have in fact done so, and the section which follows outlines the methods employed, and discusses their validity.

In all cases the splitting of the lowest energy triplet term is a function of *Dt* alone, and *Dt* may be directly determined as 4/35s of this splitting. Both *Dq* and *Dt* are fourth order radial parameters and are related by the expression[3]

$$Dt = 4/7\,(Dq_{xy} - Dq_z) \qquad (1)$$

where D_{4h} molecules of the type *trans*-ML_4Z_2 are concerned. For completeness we may note that for C_{4v} molecules of the type ML_5Z, the expression is[3]

$$\begin{aligned} Dt &= 2/7\,(Dq_{xy} - Dq_z) \\ Dq_{xy} &= Dq_L = \text{In-plane (xy) ligand field strength} \qquad (2) \\ Dq_z &= \text{out-of-plane (z) ligand field strength} \end{aligned}$$

if the simplifying assumption is made that the L ligand lying on the z axis exerts the same field as the L ligands lying in the xy plane.

In the case of tetragonal d^3 and d^8 complexes it is seen from Table 1 that the energy of the $B_{2g} \leftarrow B_{1g}$ transition, which is nearly always observed, is predicted to be equal to $10Dq_{xy}$. This prediction is confirmed experimentally[3–5]. Apparently the field in the xy plane is conserved during substitution along the z axis. It is also unaffected by configurational interaction. Therefore by combining this information with eqn. 1, it is possible to calculate the crystal field strength of the ligands along the z axis[25], Dq_z, assuming configurational interaction between the E states is absent.

$$\begin{aligned} Dq_z &= 0.1\ \mathrm{E}(B_{2g} \leftarrow B_{1g}) - 1.75\ Dt \\ &= 1/10\ (2\nu_{E_g} - \nu_{B_{1g}}) \end{aligned} \tag{3}$$

In the case of the spin-paired d^6 complexes, the transition to the corresponding orbital singlet state is also a function of the Racah parameter C, so that evaluation of Dq_z is not so straightforward. Since the field in the xy plane is conserved during substitution along the z axis, the transition to the lowest orbital singlet state will be observed at the same energy as the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition in the parent ML_6 complex (if C is unaltered).

Indeed it has been suggested[3] that more reliable Dt values are derived if Dt is calculated as 4/35s of the difference in energy between the ${}^1E_g \leftarrow {}^1A_{1g}$ transition in the tetragonal complex and the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition in the parent complex. In view of the other errors in this method, this viewpoint is not really justified.[4] Since the ${}^1A_{2g} \leftarrow {}^1A_{1g}$ transition does generally lie close in energy to the parent ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition, the variation in Dt according to the method of the calculation is small. To evaluate Dq_{xy} and hence Dq_z, it is necessary to calculate C. This is usually done by referring back to the parent complex ML_6 and assuming that the Racah parameters do not change. If the spin-forbidden transition to the ${}^3T_{1g}$ level can be observed, then, since its energy is $10Dq_{xy} - 3C$, C may be directly evaluated as one half the energy separation between this transition and the first spin-allowed transition. Failing this, the energy separation between the two spin-allowed transitions in the parent complex is approximately 16B. If the assumption is made that C = 4B, then both Dq_{xy} and Dq_z may be evaluated. This is a common assumption, but certainly does not seem to be valid for the compounds analysed by Wentworth and Piper[2], who found the ratio to be greater than 7. The method is therefore unreliable.

For d^6 compounds

$$Dq_z = 0.1\ (\mathrm{E}({}^1A_{2g} \leftarrow {}^1A_{1g}) + \mathrm{C}) - 1.75\ Dt \tag{4}$$

Table 2 lists Dq_z values calculated from eqns. 3 and 4, for a series of chromium(III) cobalt(III) and nickel(II) complexes.

Accepting the validity of the calculations for the moment, a number of general conclusions may be made about the data.

a) In the absence of steric hindrance between the ligands, Dq_{xy} in most cases lies fairly close to the value of Dq observed in the parent ML_6 complex, whilst Dq_z lies fairly close to, but in general somewhat smaller than, the value of Dq observed in the octahedral complex MZ_6 where known. Where the complexes ML_6 and MZ_6 are not known, the computed values seem reasonable.

b) When the in-plane ligand is bulky and there is likely to be inter-ligand steric

TABLE 2

IN-PLANE AND OUT-OF-PLANE FIELD STRENGTHS IN SOME TETRAGONAL CHROMIUM(III) COBALT(III) AND NICKEL(II) COMPLEXES

	Complex	Dq_{xy}	Dt	Dq_z	Z
$\mathrm{Cr^{III}}$	Cr(Ethylenediamine)$_2$(H$_2$O)$_2^{3+}$	2247	319	1689	$\mathrm{H_2O}$
	Cr(Ethylenediamine)$_2$Cl$_2^+$	2188	496	1320	Cl
	Cr(Ethylenediamine)$_2$I$_2^+$	2179	573	1177	Br
	Cr(Ethylenediamine)$_2$Br$^+_2$	2100	531	1170	I
	Cr(Ethylenediamine)$_2$(OH)$_2^+$	1992	191	1638	OH
	Cr(Bipyridyl)$_2$Cl$_2^+$	2247	506	1357	Cl
$\mathrm{Co^{III}}$	Co(Ethylenediamine)$_2$F$_2^+$	2500	619	1416	F
	Co(Ethylenediamine)$_2$Cl$_2^+$	2412	728	1138	Cl
	Co(NH$_3$)$_4$Cl$_3^+$	2278	583	1258	Cl
$\mathrm{Ni^{II}}$	Ni(Ethylenediamine)$_2$(H$_2$O)$_2^{2+}$	1370	445	590	$\mathrm{H_2O}$
	Ni(*N*,*N*-Dimethylen)$_2$(NO$_2$)$_2$	1095	253	653	$\mathrm{NO_2}$
	Ni(*N*,*N*-Dimethylen)$_2$(NO$_3$)$_2$	1185	458	383	$\mathrm{NO_3}$
	Ni(*N*,*N*-Dimethylen)$_2$(Cl$_3$C.CO$_2$)$_2$	1100	274	620	$\mathrm{Cl_3C.CO_2}$
	Ni(*N*,*N*-Diethylen)$_2$(H$_2$O)$_2^{2+}$	1045	335	459	$\mathrm{H_2O}$
	Ni(*N*,*N*-Diethylen)$_2$(NO$_2$)$_2$	1035	283	539	$\mathrm{NO_2}$
	Ni(*N*,*N*-Diethylen)$_2$(Cl$_3$C.CO$_2$)$_2$	989	267	521	$\mathrm{Cl_3C.CO_2}$
	Ni(*N*,*N*,*N*,*N*,-Tetramethylen)$_2$(NO$_2$)$_2$	1000	229	600	$\mathrm{NO_2}$
	Ni(3-Chloroaniline)$_4$(ClO$_4$)$_2$	1100	274	620	$\mathrm{ClO_4}$
	Ni(Aniline)$_4$(ClO$_4$)$_2$	1130	320	570	$\mathrm{ClO_4}$
	Ni(3-Methylaniline)$_4$(ClO$_4$)$_2$	1150	377	490	$\mathrm{ClO_4}$
	Ni(4-Methylaniline)$_4$(ClO$_4$)$_2$	1170	423	430	$\mathrm{ClO_4}$
	Ni(3-Bromopyridine)$_4$(ClO$_4$)$_2$	1160	320	600	$\mathrm{ClO_4}$
	Ni(4-Ethylpyridine)$_4$(ClO$_4$)$_2$	1140	297	620	$\mathrm{ClO_4}$
	Ni(Acetonitrile)$_2$Cl$_2$	660 (Cl)	−189	990	$\mathrm{CH_3CN}$
	Ni(Pyridine)$_2$Cl$_2$	600 (Cl)	−274	1080	Pyridine
	Ni(Quinoxaline)Cl$_2$	604 (Cl)	−176	912	Quinoxaline
	Ni(Thiourea)$_4$Cl$_2$	820	126	600	Cl
	Ni(Thiazole)$_4$Cl$_2$	1006	203	650	Cl
	*Ni(Benzimidazole)$_4$Cl$_2$ (295 °K)	1140	388	460	Cl
	(80 °K)	1210	423	470	Cl
	Ni(Pyridine)$_2$Br$_2$	580 (Br)	−251	1020	Pyridine
	*Ni(Benzimidazole)$_4$Br$_2$	1190	468	370	Br

*Acetone solvated

hindrance, then the value of Dq_z is reduced markedly. It is interesting in this context to compare nickel complexes of methyl and ethyl substituted ethylenediamines. The former being the least bulky ligand has the higher in-plane ligand field strength and gives rise to the higher out-of-plane ligand field strengths for a given z ligand[4]. The method does not appear to give realistic values of Dq_z if the in-plane ligand is macrocyclic. The implications of this will be discussed further below.

Molecular orbital interpretations have been developed by Yamatera[6] and by McClure[7]. In these the splitting of the orbital triplet states is expressed in terms of the quantities $d\sigma$ and $d\pi$.

$d\sigma$ is the difference between the σ antibonding power of the $Z(\sigma_z)$ ligand and the σ antibonding power of the (parent) ligand in the xy plane, σ_L. dπ is similarly defined, thus:

$$\begin{aligned} d\sigma &= \sigma_z - \sigma_L \\ d\pi &= \pi_z - \pi_L \end{aligned} \tag{5}$$

When we replace a ligand L in the parent complex ML_6 by a ligand Z, then we alter the energy levels by amounts proportional to these parameters. If Z is a stronger base than L, then dσ is expected to be positive, if Z is weaker than dσ is negative. Similarly if Z is more strongly π-antibonding than L, dπ will be positive. For example if Cl^- is substituted into the complex $M(NH_3)_6$ to give $M(NH_3)_4Cl_2$, then dσ should be negative since Cl^- is a weaker base than NH_3, but dπ should be positive since Cl^- has π-antibonding lone pairs, whilst NH_3 does not.

Calculation of these molecular orbital parameters is more satisfying in that the results should be more directly relateable to changes in the bonding capabilities of the various ligands. Unfortunately the splitting of the lowest energy band is a function of both dσ and dπ, so that it is not possible to derive both dσ and dπ independently unless splitting is observed in one of the higher excited states. To equate the splitting in a higher excited state to zero because it is not observed in the room temperature spectrum will yield a solution for dσ and dπ but it will be grossly unreliable. In certain cases it has been possible to derive accurate values of both dσ and dπ; these will be discussed later.

Whilst the evaluation of these molecular orbital parameters is purely empirical, other authors[8–13] have utilised an approximate LCAO MO approach called the Angular Overlap Model, to account for the d orbital energies in a metal complex. In this model the anti-bonding contribution to the energy of a given orbital is proportional to the square of its group overlap integral with the ligands. This differs from the above mentioned procedure in that it should be possible to directly calculate the energies and hence predict the splitting energies. The energies may be expressed in terms of the radial λ-antibonding parameters $e_{\lambda q}$ where $\lambda = \sigma$, π or δ, and q = x,y or z. Thus $e_{\sigma x}$ is the sum of the σ antibonding contributions

TABLE 3

ONE ELECTRON ENERGY CONTRIBUTIONS TO THE ENERGIES OF THE COMPONENTS OF THE FIRST TWO SPIN-ALLOWED TRANSITIONS IN THE SPECTRA OF *trans*-ML_4Z_2 COMPLEXES OF d^3 AND d^8 IONS

$B_{2g} \leftarrow B_{1g}$	$3e'_{\sigma L} - 4e'_{\pi L}$	Splitting of T_{2g}(F) Level
$E_g \leftarrow B_{1g}$	$\frac{3}{2}e'_{\sigma L} + \frac{3}{2}e'_{\sigma Z} - 2e'_{\pi L}$	$\frac{3}{2}e'_{\sigma L} - \frac{3}{2}e'_{\sigma Z} + 2e'_{\pi Z} - 2e'_{\pi L}$
	$-2e'_{\pi Z}$	$= -2d\sigma + 2d\pi$
$A_{2g} \leftarrow B_{1g}$	$e'_{\sigma L} + 2e'_{\sigma Z} - 4e'_{\pi L}$	Splitting of T_{1g}(F) Level
		$-\frac{3}{2}e'_{\sigma L} + \frac{3}{2}e'_{\sigma Z} + 2e'_{\pi Z}$
$E_g \leftarrow B_{1g}$	$\frac{5}{2}e'_{\sigma L} + \frac{1}{2}e'_{\sigma Z} - 2e'_{\pi Z}$	
		$- 2e'_{\pi L}$
	$-2e'_{\pi L}$	$= +2d\sigma + 2d\pi$

from each end of the x axis. In the complexes ML_4Z_2 under discussion, we may write $e_{\lambda L}$ in place of $e_{\lambda x}$ and $e_{\lambda y}$. It transpires that all the energies may be expressed in terms of the parameters $e'_{\lambda q}$ where $e'_{\lambda q} = e_{\lambda q} - e_{\delta q}$. since the observed data always involve energy differences.

The splitting of the various excited states for the complexes under discussion are given in Table 3. More complete data are given elsewhere.[13] Whilst it is possible in principle to directly calculate the transition energies utilising this approach, this has not yet been done for tetragonal complexes.

An empirical evaluation of the parameters is possible in certain cases. In general we have four unknown radial integrals and an unknown value of B, so that at least five pieces of independent information are needed.

The positions of the various transitions may be expressed in terms of these five parameters; if at least five of the six possible transitions are observed, then the parameters may be evaluated. Further simplification is possible if one of the ligands does not have any π propensity. Thus in the complex *trans*-$Ni(NH_3)_4(NCS)_2$, $e'_{\pi L}$, *i.e.* $e'\pi_{NH_3}$ may be written as zero, thus reducing the number of parameters to four.

The crystal field and angular overlap models are related by the following equations:

$$Dq = \tfrac{1}{10}(3e'_{\sigma L} - 4e'_{\pi L}) \tag{6}$$
$$Ds = \tfrac{2}{7}(e'_{\sigma L} + e'_{\pi L} - e'_{\sigma Z} - e'_{\pi Z}) \tag{7}$$
$$Dt = \tfrac{2}{35}(3e'_{\sigma L} - 4e'_{\pi L} - 3e'_{\sigma Z} + 4e'_{\pi Z}) \tag{8}$$

The equations 6, 7 and 8 would suggest that the molecular orbital and crystal field approaches are homomorphous. However, this is not strictly true in the sense that the constraints placed upon $e'_{\sigma L}$, for example, by the σ-antibonding nature of the ligands are not the same constraints as those imposed upon the radial integrals by the crystal field model.

In the d^3 and d^8 complexes the transition to the B_{2g} level identifies $10Dq_{xy}$, thus in the nickel complex cited above, and utilising eqn. 6, $e'_{\sigma NH_3}$ may be directly evaluated as one third the energy of this transition. The observed splittings of the first two spin-allowed transitions provides the necessary additional information to solve for the remaining radial parameters. The resulting data (column 2, Table 4) indicate that the thiocyanate group is a slightly stronger σ bonding ligand than ammonia, and is also a more strongly π anti-bonding ligand, in this complex. This last point is especially interesting since it indicates that the filled π orbitals of the NCS group interact with the nickel d orbitals, and that this interaction is more important that a possible π bonding interaction between the metal d electrons and the empty π- anti-bonding orbitals of the NCS group. This particular approach is obviously of considerable importance and utility, and it will be interesting to see if further work will confirm its validity.

In many complexes, particularly those of macrocyclic ligands, the field can hardly be regarded as weak and a 'strong field' approach (iii) to the problem might seem more appropriate.

A d orbital energy level sequence is set up. This is shown in Fig. 4, with appropriate labelling of the energy separations. These are chosen so that the calculated Δ_1 and Δ_3 values are directly equal to the splittings of the t_{2g} and e_g levels in the cubic parent, whilst Δ_2 is equal to $10Dq_{xy}$. Assuming the energy order indicated, the ground state is, as before, B_{1g}, for d^3 and d^8 ions. The energies of the states, relative to the ground state as zero, are:

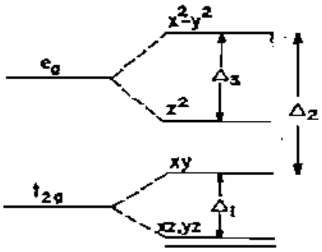


Fig. 4. Splitting of the d orbitals in a tetragonal field of D_{4h} symmetry.

$$\begin{array}{ll}
B_{1g} & 0 \\
A_{2g}{}^{a} & \Delta_2-\Delta_3+12B \\
B_{2g} & \Delta_2 \\
E_g{}^{a} & \Delta_1+\Delta_2-\Delta_3+3B \\
E_g{}^{b} & \Delta_1+\Delta_2+9B \\
E_g{}^{c} & \Delta_1+2\Delta_2-\Delta_3+3B \\
A_{2g}{}^{b} & 2\Delta_1+2\Delta_2-\Delta_3+3B
\end{array} \tag{9}$$

The solutions to these equations are given for $Ni(NH_3)_4(NCS)_2$, $Ni(Py)_4Cl_2$ and $Ni(Py)_4Br_2$ in column 1 of Tables 4–6. The low temperature spectra[14,15] of these compounds were used, since these exhibit a splitting of all three orbital triplet states.

The strong and weak field parameters are linked by the following relationships:

$$\Delta_1 = 3Ds-5Dt \qquad \Delta_2 = 10Dq_{xy} \qquad \Delta_3 = 4Ds+5Dt \text{ or}$$
$$7Ds = \Delta_1+\Delta_3 \qquad -35Dt = 4\Delta_1-3\Delta_3 \tag{10}$$

Moreover there are further relationships linking the crystal field parameters to the molecular orbital parameters:

$$\begin{aligned}
8d\sigma &= -12Ds-15Dt \\
2d\pi &= -3Ds+5Dt \\
8d\sigma - 8d\pi &= -35Dt \\
8d\sigma + 6d\pi &= -21Ds
\end{aligned} \tag{11}$$

TABLE 4

CALCULATED PARAMETERS FOR $Ni(NH_3)_4(NCS)_2$ [CM^{-1}]

Parameter	*Strong*[b]	*Weak*[c]	*+C.I.*[d]
Dq_L	1075	1075	1075
Dq_Z	7340	1075	1103
$\Delta 1$	−78	−75	−250
$\Delta 3$	2154	−100	−521
B	742	932	847
dσ	−806	38	195
dπ	38	38	125
Dt	193	0	−16
Ds	296	−25	−110
$e'_{\sigma NH_3}$	3583	3583	3583
$e'_{\pi NH_3}$	0[a]	0[a]	0[a]
$e'_{\sigma NCS}$	2508	3633	3843
$e'_{\pi NCS}$	38	38	125

[a] Assumed. [b] No C.I. [c] C.I. between T_{1g} states in O_h included. [d] All C.I. included. C.I. configurational interaction.

Using the parameters in the right hand column

	$E_g{}^a$	B_{2g}	$A_{2g}{}^a$	$E_g{}^b$	$A_{2g}{}^b$	$E_g{}^c$
Calculated Transition energies	10,888	10,750	17,500	17,167	28,000	27,945 cm^{-1}
Observed Transition energies	10,750	10,750	17,500	17,350	28,000	27,900 cm^{-1}

TABLE 5

CALCULATED PARAMETERS FOR Ni (PYRIDINE)$_4$Cl$_2$, [CM^{-1}]

Parameter	*Strong*[a]	*Weak*[b]	*+C.I.*[c]
Dq_L	1173	1173	1173
Dq_Z	474	634	673
$\Delta 1$	−402	−403	147
$\Delta 3$	4120	3056	3528
B	610	395	821
dσ	−1545	−1146	−1323
dπ	201	201	−73
Dt	399	308	286
Ds	531	379	525

[a] No C.I. [b] C.I. between T_{1g} states in O_h included. [c] All C.I. included.

Using the parameters in the right hand column

	$E_g{}^a$	B_{2g}	$A_{2g}{}^a$	$E_g{}^b$	$A_{2g}{}^b$	$E_g{}^c$
Calculated Transition energies	9000	11,730	14,930	16,874	25,812	26,745
Observed Transition energies	9042	11,730	14,930	16,818	?	26,759

TABLE 6

CALCULATED PARAMETERS FOR Ni (PYRIDINE)$_4$Br$_2$, [CM^{-1}]

Parameter	*Strong*[a]	*Weak*[b]	*+C.I.*[c]
Dq_L	1149	1149	1149
Dq_Z	408	536	596
$\Delta 1$	−374	−376	330
$\Delta 3$	4442	3582	4125
B	586	352	810
dσ	−1665	−1343	−1547
dπ	186	188	−165
Dt	423	350	316
Ds	581	458	636

[a] No C.I. [b] C.I. between T_{1g} states in O_h included. [c] All C.I. included.

Using the parameters in the right hand column

Calculated	E_g[a]	B_{2g}	A_{2g}[a]	E_g[b]	A_{2g}[b]	E_g[c]
Transition energies	8420	11,490	14,080	16,400	24,950	26,040
Observed						
Transition energies	8430	11,490	14,080	16,390	?	26,030

$$
\begin{aligned}
d\sigma &= -\tfrac{3}{8}\Delta_3 \\
d\pi &= -\tfrac{1}{2}\Delta_1
\end{aligned}
\qquad (12)
$$

The molecular orbital parameters are inter-related by:

$$
\begin{aligned}
d\pi &= e'_{\pi Z} - e'_{\pi L} \\
d\sigma &= \tfrac{3}{4}\,(e'_{\sigma Z} - e'_{\sigma L})
\end{aligned}
\qquad (13)
$$

Eqns (10)–(13) only apply to high spin *trans* ML_4X_2 complexes, (M, A_{2g}(F) ground state in O_h). In general they will differ for other systems.

How different are the results obtained using weak field free ion wavefunctions versus using the strong field wavefunctions as our basis set? By using the relationships previously defined, the two calculations may be directly compared. The results for the three complexes mentioned above are given in columns 1 and 2 of Tables 4–6.

The agreement between the two sets of data is not very good, and is especially bad for the ammino complex. Of course there is no reason why the two sets of data should tally – but which, if either, is closer to reality? Before answering this point we might consider whether the parameters have values which are chemically intuitively reasonable. First the pyridine complexes- dσ is negative and becomes more negative in passing from the chloride to the bromide. This is acceptable on the basis of the relative base strengths of chloride and bromide *versus* pyridine, dπ is positive and its variation implies decreasing π donation to the nickel atom in the sequence Cl > Br > pyridine. As a consequence of the sign of dπ, Δ_1 is negative, *i.e.* our energy level diagram (Fig. 5) should have the d_{xy} level *lower* than the d_{xy}, d_{yz} levels, and the splitting of the t_{2g} level is in a contra-crystal field sense[16].

Such an order is acceptable if π-donation from the halogens is taken into account. Δ_3 is a moderately large positive quantity, implying a moderately strong tetragonal perturbation to the 'octahedral' field. Dq_z, the crystal field strength of the halogen, turns out to have a reasonable value using the weak field approach, but an unreasonably small value in the strong field approach. The Racah B values tend to be low, especially in the weak field case. In the ammino complex some of the parameters (Ds, $d\sigma$ and Δ_3) turn out to bave opposite signs in the two approximations.

In order to decide which of these two approaches was the most realistic, the parameters were re-determined after taking into account the interaction between the three E_g levels and between the two A_{2g} levels. Thus with configurational interaction included, the energies of the six transitions are given by a linear equation, a two by two secular determinant and a three by three secular determinant.

The energies of the states, relative to $E(B_{1g}) = 0$, are:

$$\begin{array}{ll} B_{2g} & \Delta_2 \\ A_{2g}{}^{a}, A_{2g}{}^{b} & \begin{vmatrix} \Delta_2-\Delta_3+12B-E & 6B \\ 6B & 2\Delta_1+2\Delta_2-\Delta_3+3B-E \end{vmatrix} = 0 \\ E_b{}^{a}, E_g{}^{b}, E_g{}^{c} & \\ & \begin{vmatrix} \Delta_1+\Delta_2-\Delta_3+3B-E & +3\sqrt{3}B & -3B \\ +3\sqrt{3}B & \Delta_1+\Delta_2+9B-E & -3\sqrt{3}B \\ -3B & -3\sqrt{3}B & \Delta_1+2\Delta_2-\Delta_3+3B-E \end{vmatrix} = 0 \end{array} \tag{14}$$

These equations should provide a complete description of the spectrum of any d^3 or d^8 complex in a tetragonal environment, (assuming the ground state is B_{1g}).

An analysis of a spectrum using these equations is a little more time consuming than using the first-order equations, but may be made fairly rapidly by noting that Δ_2 is, as always, given by the $B_{2g} \leftarrow B_{1g}$ transition energy, and that

$$\Delta_1 = \Sigma E_g - \Sigma A_{2g} - \Delta_2 \tag{15}$$

where ΣE_g and ΣA_{2g} are the sums of the observed transitions to the three E_g states and to the two A_{2g} states, respectively.

Since

$$2\Delta_1+3\Delta_2-2\Delta_3+15B = \Sigma A_{2g} \tag{16}$$

(the sum of the roots of a secular determinant is equal to the sum of the diagonal elements), it is possible to express Δ_3 as a function of B.

One of the A_{2g} energies is inserted into the two by two determinant, together with Δ_3 as a function of B, and numerical values of Δ_1 and Δ_2, to provide a solution for B. The resulting values of Δ_1, Δ_2, Δ_3 and B, derived should be inserted into the three by three secular determinant, which is then solved to produce the three E_g transition energies. Remarkably good agreement between the observed and calculated spectra, with regard to wavelength at least, are obtained. If only the B_{2g} and the three E_g transitions are observed, then these three E_g energies may be used to solve the 3×3 determinant for Δ_1, Δ_3 and B directly. However such a procedure is very time consuming unless a computer program is available.

The results of the complete calculation for the three nickel complexes are given in column 3 of Tables 4–6. Rowley and Drago[15] have made a complete calculation using weak field functions as their basis set, and expressing the equation in terms of Ds, Dt, Dq and B. A similar calculation has been published by Krishnamurthy, Schaap and Perumareddi,[17] who utilised the data for a discussion of tetragonal chromium(III) derivatives. The equations whilst expressed in terms of Ds, Dt, Dq and B are quite analogous to those reported here(14).

Comparison of the results of the complete calculation with those of the weak field calculation which has generally been used in the past, and which takes into account configurational interaction between the parent octahedral T_{1g} levels shows that the inclusion of configurational interaction between A_{2g} and between E_g levels does not greatly affect the evaluation of Dt, and hence of Dq_z, but may materially alter the other parameters. Hence the Dq_z data given in Table 2 where configurational interaction between the A_{2g} and between the E_g states was ignored, may be accepted as approximately valid. If Dt is positive, then the E_g^a state lies below the B_{2g} state. Configurational interaction will tend to depress the E_g^a level further so that Dt will appear larger (and Dq_z smaller) than it really is. Thus for complexes with Dt positive, the Dq_z data given in Table 2 should be increased by a few percent. We had already noted that the Dq_z values for sterically unhindered complexes seemed a trifle low.

When Dt is negative the E_g^a state lies above B_{2g}. Configurational interaction will depress the E_g level, thus making Dt appear smaller than it really is. A negative increase in Dt will once again lead to an increase in Dq_z. Hence all the Dq_z values in Table 2 should be increased by a few percent. The discrepancy will be a minimum for the stronger field ligands where the E_g energy levels are comparatively far apart, and for the more covalent ligands where the smaller value of B will depress the interelectronic repulsion and hence the interaction of the E_g levels. Note that in the case of the $Ni(NH_3)_4(NCS)_2$ complex, configurational interaction has depressed the E_g^a level until it is coincident with the B_{2g} level, no splitting being observed. Despite the absence of splitting, the thiocyanate group has a stronger crystal field than ammonia and Dt is non-zero.

Referring to the complete calculation on the nickel pyridine derivatives, column 3, Tables 4–6, Δ_1 is now seen to be positive, and $d\pi$ negative. This is predicted by the crystal field model, but is difficult to explain on the molecular orbital model. To do so requires that the chloride ion be an effective π acceptor or the pyridine an effective π donor. Neither postulate seems very reasonable. The other parameters have values whose significance is as discussed earlier. The ammino complex has negative values for both Δ_1 and Δ_3, implying that the splitting of both the t_{2g} and e_g levels is inverted. The thiocyanate group turns out to have a slightly stronger field than the ammonia group explaining the order $d_{x^2-y^2} < d_{z^2}$. This of course gives a positive value for $d\sigma$. The positive value of $d\pi$ appears to indicate that the thiocyanate group is an effective π donor rather than a π acceptor.

If we assume that $e'_{\pi NH_3}$ is zero, than it is a straightforward calculation to obtain the other angularoverlap parameters. $e'_{\sigma NCS}$ is slightly greater than $e'_{\sigma NH_3}$ in agreement with the weak field result, $e'_{\pi NC}$ is positive, meaning that the NCS group exerts a π anti-bonding effect, *i.e.* is a π-donor. This is not, of course, a proof of the earlier statement, since the various relationships linking the different parameters, assured that this result would be obtained.

TABLE 7

CALCULATED PARAMETERS FOR SOME CHROMIUM(III) DERIVATIVES [CM^{-1}]

Parameter	$Cr(en)_2(H_2O)_2^{3+}$	$Cr(en)_2Cl_2^+$	$Cr(en)_2Br_2^+$	$Cr(H_2O)_4F_2^+$
Dq_L	2247	2188	2179	1740[a]
Dq_Z	1690	1327	1192	1544
$\Delta 1$	−2495	−3330	−3575	850
$\Delta 3$	384	1296	1812	2439
B	632	593	581	645
$d\sigma$	−144	−486	−679	−915
$d\pi$	1247	1665	1787	−425
Dt	318	492	564	112
Ds	−302	−291	−252	470
$e'_{\sigma N}$	7490	7293	7263	
$e'_{\pi N}$	0[a]	0[a]	0[a]	
$e'_{\sigma Z}$	7298	6645	6358	
$e'_{\pi Z}$	1247	1665	1787	
Z^*	1.35	1.2	1.1	1.35

Spectral data from Baker and Phillips, *Inorg. Chem.*, 5 (1966) 1042.
Calculated assuming configurational interaction between E_g^a and E_g^b only. [a]Assumed.

Table 7 illustrates the data obtained from a calculation of the spectra of some chromium ethylenediamine derivatives. A gaussian analysis of the spectra[18] revealed the energies of the components of the ${}^4T_{2g}$ and ${}^4T_{1g}$ (F) levels. The components of the ${}^4T_{1g}$ (P) level were not observed, being too high in energy. The calculation was carried out assuming configurational interaction between the two observed E_g states (E_g^a and E_g^b). E_g^c was assumed to have a negligible effect on their energies, being of too high an energy. The Dq_z and Dt values obtained were almost identical to those derived from weak field treatment in which the E interaction was ignored. The Δ_3, $d\sigma$ and $e'_{\sigma Z}$ values vary in agreement with a decreasing σ bonding interaction in the sequence $H_2O > Cl > Br$, as would be predicted.

Δ_1 is negative, and $d\sigma$ positive, implying a reversal of the splitting of the t_{2g} level. This is due to a progressively stronger π-donor interaction from the axial ligand in the sequence $H_2O < Cl < Br$, as indicated by the angular overlap parameters. Since the complex *trans* $Cr(H_2O)_4F_2^+$ has a negative value for $d\pi$, it follows that we may place F at the beginning of the above sequence being a poorer π-donor towards chromium(III) than water.

Note that Dq_L is almost independent of the axial ligand; however the aquo complex does have a significantly higher value for the crystal field strength of the ethylendiamine ligand, than do the other complexes. This may be accredited to the higher effective nuclear charge on the chromium atom as indicated in a qualitative manner by the value of B. Approximate values of Z^*, the effective nuclear charge, are given in Table 7. These are based on the value of B[1,2,19].

An extensive series of tetragonal metal complexes exists in which the in-plane ligand is a tetradentate macrocyclic group such as *cyclam*, *pex*, or CTH (Fig. 5). Many cobalt(III) and nickel(II) complexes containing the chromophore M(macrocycle)X_2 have been synthesized and their spectra reported[20-23]. The cobalt(III) complexes frequently exhibit a splitting of the first spin-allowed band; however since spin-forbidden transitions are rarely observed and the corresponding parent octahedral complexes are unknown, it is not generally possible to evaluate C. For this reason an analysis of the complex in a systematic manner is not possible, and we will not consider the complexes further here.

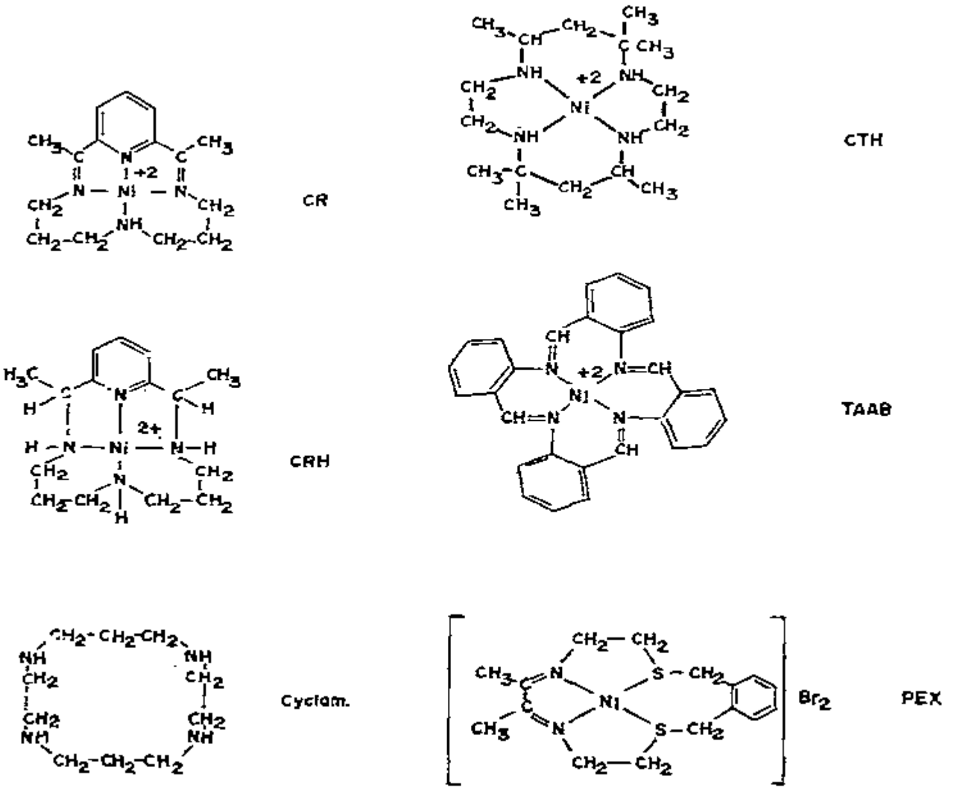


Fig. 5. Some macrocyclic ligands capable of forming tetragonal complexes with nickel(II).

The nickel complexes of this type fall into two classes, those which are paramagnetic and those which are diamagnetic. The paramagnetic complexes exhibit spectra which are often quite dissimilar from those discussed for the simpler ligands. In some cases there is an apparent splitting of the first band and a value for Dt may be derived. Some data is given in Table 8. The nickel *pex* complexes yield Dq_z values for chloride and bromide distinctly above those observed in the corresponding NiZ_6 complexes. These will rise even higher when configurational interaction is taken into account. Whilst it does not necessarily follow that Dq_z as determined in the NiZ_6 complexes is a maximum value (inter-ligand repulsion, for example, may yield a slightly longer metal halogen distance than the electronic energies would require) the data are rather difficult to explain. The in-plane field

TABLE 8

OBSERVED TRANSITION ENERGIES AND CALCULATED PARAMETERS FOR MACROCYCLIC NICKEL(II) *PEX* COMPLEXES, (ALL DATA IN CM^{-1})[28,29]

Complex	γ_a	γ_b	γ_c	γ_d	Dq_{xy}	Dt	Dq_Z	Z
Ni(pex)Br_2	9.01	10.2	16.2	22.7	1020	136	782	Br
Ni (pex)Cl_2	9.28	10.7	18.4	24.8	1070	163	786	Cl
Ni(pex)$(N_3)_2$	9.90	10.8	19.9	26.8	1080	103	900	N_3
Ni(pex)(NCS)$_2$	11.7	10.8	18.4	24.0	1080	−103	1260	NCS

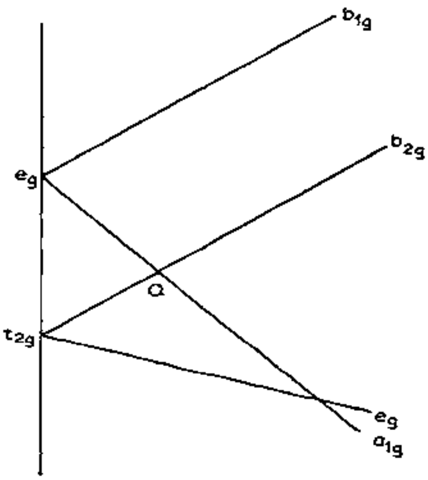


Fig. 6. Energy level diagram for tetragonal d^8 complexes
d^8 $^3B_{1g}$ $(e)_g^4(b_{2g})^2(a_{1g})(b_{1g})$
$^3A_{2g}$ $(e_g)^4(a_{1g})^2(b_{2g})(b_{1g})$
$E(^3A_{2g})-E(^3B_{1g}) = \Delta_2-\Delta_3+12B$
Change of ground state occurs when $\Delta_3 > \Delta_2+12B$.

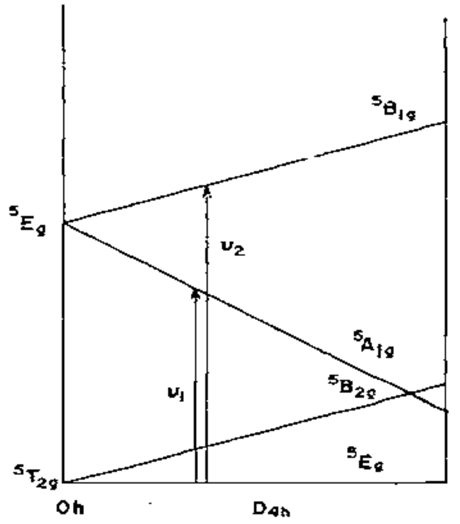


Fig. 7. Energy level diagram for *trans* FeL_4Z_2 complexes ($Dq_z < Dq_L$)
$\nu_1 = 10Dq_{xy}-Ds-10Dt$
$\nu_2 = 10Dq_{xy}+3Ds-5Dt$
Splitting $= \nu_2-\nu_1 = 4Ds+5Dt = -8/3\ d\sigma$

strengths are approximately independent of the axial ligand as anticipated. In fact with the exception of the bromide, the in-plane field is constant to within experimental error. Since the spectrum of the bromide was obtained in solution, whilst the other spectra were recorded in the solid state, the bromide value is not really comparable with the others.

However few of the macrocyclic complexes behave as well as *pex*. Reference to Fig. 8 and 9 shows that there is no band clearly independent of the axial ligand[26,29]; all the bands seem to vary with change of the z ligand.

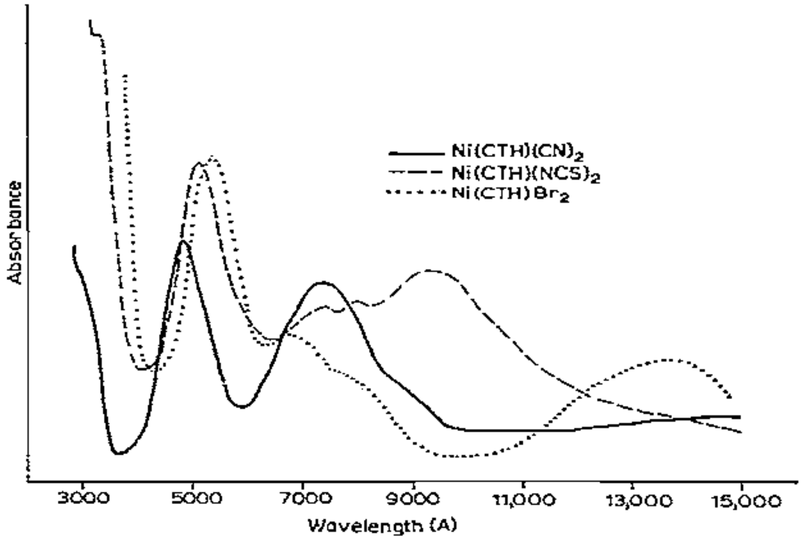


Fig. 8. Electronic absorption spectra of some typical α-Ni(CTH)X$_2$ derivatives[26].

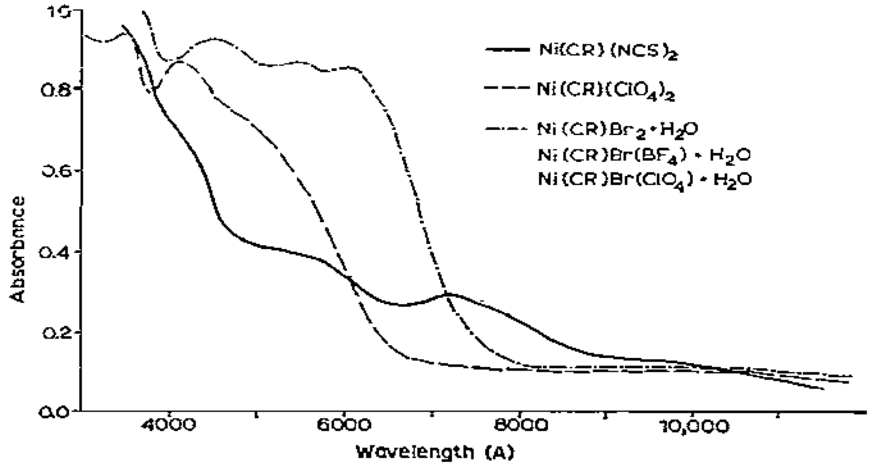


Fig. 9. Electronic absorption spectra of some typical Ni(CR)X$_2$ derivatives[16].

According to crystal field theory substitution along the z direction should have no effect upon the in-plane field. In practice we find this to be generally true for simple ligands. But need it always be true? Clearly if the in-plane ligands can exert a steric effect upon the axial ligands the converse should be true. Bulky axial ligands may cause a lengthening in the in-plane metal ligand bond. In molecular orbital terms a *cis* effect might also be anticipated in which the axial metal ligand bonds influence the equatorial metal ligand bonds through an electronic mechanism. In fact the observation of in-plane field independence in the more simple complexes implying that the molecules adhere to the crystal field theory rather than ligand field theory is really rather remarkable, and on sober analysis might not have been predicted. The macrocyclic complexes may therefore be examples of normal rather than abnormal behaviour. Indeed there may well be changes in the conformation of the macrocycle from one complex to another giving rise to changes in Dq_{xy}. The positions of the absorption bands are not well predicted by theory in these complexes and it is necessary to re-investigate the basic premise that these molecules do possess a $^3B_{1g}$ ground state. In any tetragonal nickel(II) complex as the axial field strength decreases, or, more to the point, as the difference between the in-plane and out-of-plane field increases, there comes a point when there is a changeover to a diamagnetic molecule. Many of the iodide and perchlorate complexes with in-plane ligands of the type indicated in Table 2 are diamagnetic. In some cases even the bromides are. This is a consequence of the low crystal field strengths of these particular groups. These diamagnetic complexes may be square planar (axial field strength zero), or more likely tetragonal with long metal to axial ligand bonds. Is it possible that prior to this changeover in spin-state, there is another changeover to another orbital state but still with triplet spin?

Reference to Fig. 6 shows that there will be a point, as the splitting of the e_g levels increases, *i.e.* as Δ_3 increases, when a changeover in ground state should occur. It is evident that the excited $^3A_{2g}$ state can become the ground state if $\Delta_3 > \Delta_2 + 12B$, *i.e.* if Δ_3 is of the order of 20,000 cm^{-1} (probably somewhat less when configurational interaction is taken into account). This is a very considerable splitting. In fact it turns out that the molecule is likely to go diamagnetic before the $^3A_{2g}$ level becomes the ground state. Neglecting configurational interaction, a change in magnetic state, to the singlet will occur if $\Delta_3 > 12B + 3C$, which is of the order of 19,000 cm^{-1}. This value also decreases if C.I. is taken into account. It is also conceivable that the $^3E_g^a$ state could become the ground state. This will occur when $\Delta_3 > \Delta_1 + \Delta_2 + 3B$. Since $d\pi$ is likely to be positive in the complexes under discussion, (the macrocycle will very likely have an $e'_{\pi L}$ value of zero, whilst $e'_{\pi z}$ will probably be positive), Δ_1 will be negative. Hence a changeover to the $^3E_g^a$ level as ground state might well occur prior to the molecule becoming diamagnetic. Attempts to solve the spectra of these complexes making this assumption are currently in progress[30].

Complexes of D state ions include derivatives of titanium(III), chromium-

(II), manganese(III), iron(II) and copper(II). Cubic molecules containing these ions might be expected to give rise to a single crystal field band corresponding to the transition between the e and t_2 levels. However in general this is not the case.

Considering octahedral molecules for example, those ions with a T_{2g} octahedral ground state (titanium(III), iron(II)) give rise to an assymetric band which may be resolved into two components. This is believed to arise through a Jahn–Teller distortion of the excited E state. In other words the equilibrium geometric configuration of the E state is not cubic and may well be tetragonal.

If we then consider the spectra of complexes whose ground states are already tetragonal, such as *trans*-$Fe(Py)_4Br_2$, we do not see much of a change in the observed spectrum. There are still two bands which may or may not be fully resolved. Table 9 lists some data for these compounds and the transitions and energies are illustrated in Fig. 7. In this figure it is assumed, for the sake of argument, that the out-of-plane field strength (Dq_Z) is weaker than the in-plane field strength (Dq_L). The energy level sequence applies strictly in the absence of π bonding which may invert the order of the lower pair of levels. The transition between these levels, which would lie in the infrared region has not been observed.

Since the energies of the bands are formulated in terms of three unknowns Dq_{xy}, Ds and Dt, and only two items of information are available, it is not possible to solve for these three parameters. If it may be assumed that the ground state is B_{2g}, then the transition to the B_{1g} level is equal as always to $10Dq_L$. For the ground state to be B_{2g} it is necessary that $d\pi$ be negative (*i.e.* Δ_3 be positive). Whilst we cannot evaluate this quantity, it would appear from consideration of the π bonding capabilities of the various ligands in Table 9 that $d\pi$ is positive in all the cases listed. Hence the ground state should be E_g. Certainly the B_{1g} band does not

TABLE 9

OBSERVED TRANSITION ENERGIES AND $d\sigma$ PARAMETER FOR SOME TETRAGONAL IRON(II) COMPLEXES

Complex	${}^5A_{1g}\leftarrow$	${}^5B_{1g}\leftarrow$	$d\sigma$
Fe(*o*-Phenanthroline)$_2$Cl$_2$	8470	10510	−765
Fe(*o*-Phenanthroline)$_2$Br$_2$	8470	10750	−855
Fe(*o*-Phenanthroline)$_2$(NCS)$_2$	9800	(12050)	−844
Fe(*o*-Phenanthroline)$_2$(N$_3$)$_2$	(10200)	(12200)	−750
Fe(Pyridine)$_4$Cl$_2$	(8550)	10300	−656
Fe(Pyridine)$_4$Br$_2$	7750	10650	−1088
Fe(Isoquinoline)$_4$Cl$_2$	(9100)	10950	−694
Fe(Isoquinoline)$_4$Br$_2$	7800	11450	−1369
Fe(Isoquinoline)$_4$I$_2$	5900	11750	−2194
Fe(3-Picoline)$_4$Br$_2$	7500	11000	−1312
Fe(Pyridine)$_2$Cl$_2$	9900	5850	+1518
Fe(Pyridine)$_2$Br$_2$	9550	5200	+1631
Fe(4-Cyanopyridine)$_2$Cl$_2$	9850	6250	+1350
Fe(4-Cyanopyridine)$_2$Br$_2$	9780	5850	+1473
Fe(3,5-Dichloropyridine)$_2$Cl$_2$	9350	6300	+1144
Fe(3,5-Dichloropyridine)$_2$Br$_2$	9050	5875	+1191

$\Delta_3 = -\frac{3}{8}d\sigma$

seem to be a constant for any of the in-plane ligands given in Table 9. It is interesting that Mossbauer experiments suggest[31] the ground state is non-degenerate. Absolute proof is lacking.

Expressed however in McClure's molecular orbital parameters, the splitting of the excited state, and hence the difference in energy of the two bands (E−A) is $-8/3\ d\sigma$. The Table evaluates $d\sigma$ whose sign is chosen on the basis of whether the in-plane or out-of-plane ligands are regarded as having the stronger base strength.

The data appear at first sight to correlate in that for a given in-plane ligand, $d\sigma$ increases as the σ bonding ability of the out-of-plane ligand decreases, *e.g.* in the sequence $Cl < Br < I$. However reference to eqn. 5 shows that the difference $d\sigma(Cl) - d\sigma(Br)$, neglecting steric phenomena, ought to be constant or nearly so, being independent of the in-plane ligand. This presupposes that the σ bonding power of the in-plane ligand is independent of the axial ligand, which we have found to be generally true for these types of ligand, and that the σ bonding power of, say, chloride, is independent of the in-plane ligand. This is also found to be approximately true in the absence of steric effects. It is clear from the Table that this difference is not a constant. It varies from 47 in the case of 3,5-dichloropyridine to 432 in the case of pyridine to 675 in the case of isoquinoline. Apparently one or both of these assumptions are incorrect, although it should be borne in mind that the difference between two large numbers is being compared. The agreement may not be as bad as it looks.

Further discussion of these complexes must await further study. The interpretation given above must be regarded as very tentative in that octahedral complexes FeL_6 also give a split band from which a value of $d\sigma$ could be derived. Its significance is uncertain. Perhaps it provides information on the difference between the short and long M–L bonds in the excited state equilibrium configuration.

For complexes whose octahedral ground state is E_g (*e.g.* chromium(II), manganese(III) and copper(II)) the ground state is subject to Jahn–Teller distortion and such complexes are generally tetragonal. The spectra generally consist of one or sometimes two bands which may be resolved into three or even four components. Since the assignment of these bands is still open to controversy and no chemical information has as yet been derived therefrom, these complexes will not be discussed further.

A similar situation obtains for octahedral complexes with T_{1g} ground states such as vanadium(III) and cobalt(II). The spectra are very complex and few definite assignments have been made.

It is evident that use of the angular overlap model in the analysis of the detailed spectra of non-cubic molecules can provide, apparently at least, some very valuable chemical information. However such studies are only in their infancy. It is clear that considerable further data are necessary in order to adequately test the theory. There is particular need for further studies in low temperature spectra and in the polarised light absorption of single crystals.

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