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ANALYTICAL TREATMENT OF THE ELECTRONIC SPECTRA OF SOME LOW-SYMMETRY TRANSITION METAL COMPLEXES

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CONTENTS

A. INTRODUCTION

In 1968 the conference proceedings of the International Symposium on the Synthetic and Stereochemical Aspects of the Chemistry of Coordination Compounds (Nara, Japan) were published in this journal. They contained an article by this author dealing with the electronic spectra of tetragonal metal complexes [1]. It seems appropriate, in this conference proceedings issue, to take another look at this area of chemistry.

There has been a very great expansion in our knowledge of the electronic spectra of low-symmetry transition metal complexes since 1968. In the space available it would not be possible to cover all of this development; moreover, a number of excellent reviews have been published in the interim period [2–4]. It is therefore proposed to consider a small slice of this problem, and deal only with those systems with which the author has been especially involved.

We will consider only fourfold, and some twofold distorted complexes leaving the special problems of threefold distortion to other colleagues. We also choose to adopt a somewhat pedagogical approach, to indicate how an absorption spectrum can lead to useful chemical information. In the first part of this contribution, the analysis of the electronic spectra of various low-symmetry complexes, is discussed. In the second part of the article, orbital angular overlap model (AOM) parameters are summarized for a series of well-defined species, and the difficulties and advantages of this approach are reviewed.

B. ANALYSIS OF THE ELECTRONIC SPECTRA OF VARIOUS LOW-SYMMETRY COMPLEXES

(i) Generation of spectroscopic data

For a definitive analysis, high-quality, single-crystal measurements using polarized light at cryogenic temperatures are essential. Such data require considerable skill to obtain and knowledge of the crystal structure of the species is highly desirable.

However, high quality and chemically useful data can often be obtained, using ordinary light, from un-oriented single crystals if such spectra are obtained at low temperatures. These data can be collected with a conventional spectrometer using a simple cryostat. Indeed, mull transmittance spectra at cryogenic temperatures can be of quite high quality. If the distortion is great enough, i.e. if there is sufficient difference between the axial and equatorial ligand fields, a resolved spectrum can be obtained with relatively little effort.

The publication of tables of room temperature solution or mull transmittance spectra, without presentation of the spectra themselves (in diagrams) is of very little value insofar as low-symmetry complexes are concerned. Other workers can gain very little of value from such presentation. Individuals working with low-symmetry complexes are urged to publish representative spectra and, where possible, to obtain such spectra at low temperatures. The accumulation of such a data base in the literature will alert other workers to the more interesting systems where X-ray structures and single-crystal polarized light studies can then be undertaken.

Where first row transition metal, F ground term ions are concerned, such spectra can contain a considerable amount of chemical information. Most effort in recent years has been devoted to complexes of chromium(III), nickel(II) and, to a lesser extent, cobalt(II). The informational content of D term ions has, with the exception of copper(II), not been significantly explored because, in general, the resolution is insufficient to allow an unequivocal analysis. The special problems and interest of low-symmetry copper(II) complexes have been reviewed [2], and will not concern us here.

If we exclude the rather small group of researchers who undertake spectroscopy for its own sake, most individuals use spectroscopy as a tool to determine, among others, the stereochemistry of a newly prepared metal complex. Clearly this is a very powerful tool which can, for example, readily distinguish octahedral from tetrahedral from square-planar nickel(II) complexes [5].

We distinguish here systems differing in a more subtle fashion, for example, six coordinate *cis*- and *trans*-ML_4Z_2 and ML_4ZZ' complexes, and five coordinate (in and out-of-plane) ML_4Z species. We also explore methods of analysing some types of complexes containing no higher than twofold symmetry, with angular or radial distortion.

(ii) Initial theoretical analysis via the Normalized Spherical Harmonic Hamiltonian (NSH) [*6*]

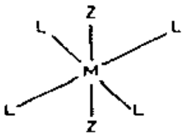
The NSH approach (using the parameters *DQ*, *DS*, *DT*, etc.) has several far-reaching advantages with respect to low-symmetry complexes when compared with the more classical crystal field approach (using *Dq*, *Ds*, *Dt*, etc. as parameters). In particular, the numerical magnitudes of the parameters are independent of the coordinate frame of axes chosen, which is not true in the classical model. Since, in low symmetry systems, the coordinate axis may not be uniquely chosen, this is an important attribute. Moreover, direct comparison can be made between sets of parameters obtained with different molecules belonging to different point groups, provided they can be related through a chain of groups. This standardization will permit the ready comparison of data from various research workers on various molecules. In addition, the form of the Hamiltonian is very simple and a single Hamiltonian, which may be looked up in a table may be applicable to a variety of molecules in different point groups (see below). The NSH approach has been reviewed in detail [6].

The main disadvantage of the NSH approach is the lack of an immediate appreciation of the *chemical* significance of the parameters; rather, they provide a group theoretical appreciation of the molecule. The "Orbital Angular Overlap" Model (AOM) [7,8], on the other hand, appears to provide an immediate assessment of the chemical bonding in the complex via use of parameters apparently more readily identified with σ and π chemical bonding, or anti-bonding.

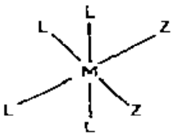
We argue here that the combined use of the NSH and AOM approaches provides a powerful means of obtaining useful chemical information from electronic spectra.

(a) Tetragonal complexes ML_4Z_2

We begin by considering the very well-known class of complexes of general formula ML_4Z_2 (where L_4 may also be represented by two bidentate ligands LL). Consider reaction of sym-diethylethylenediamine (LL) with nickel(II) or cobalt(II) dibromide to form a high spin complex of stoichiometry $M(LL)_2Br_2$ (M = Ni(II), Co(II)). In the absence of crystallographic data, electronic spectroscopy can be used to distinguish the various possible structure for this species. We anticipate from general cobalt(II) and nickel(II) chemistry, that these species may be based upon trigonal bipyramidal five-coordinate structures, or upon fourfold or twofold distorted six-, five- or four-coordinate structures. These two groups of structures have very different spectra [5] and may usually be distinguished by comparison with known members of each series [5]. Indeed these species do belong to the latter group. In this case structures A–E are most likely to represent all possible microstoichiometries for these complexes.



A



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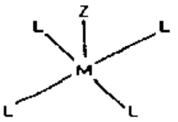
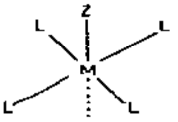


C



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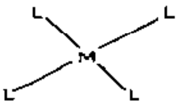

E

Complexes A, C, D, E fall into the D_{4h} or C_{4v} point groups and have the same splitting pattern as shown in Fig. 1. Most importantly complex B,

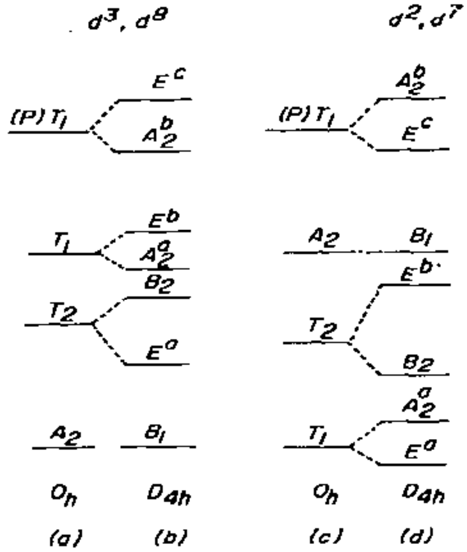

Fig. 1. Octahedral (O_h) and tetragonal (D_{4h}) splitting diagrams for group theoretical states of high spin d^7 (c, d) and d^8 (a, b).

assuming all angles are 90°, will have intermediate symmetry D_{4h} [6,9], and the diagram in Fig. 1 can still be used, albeit with different symmetry labels.

The Hamiltonian appropriate for *all* these systems (A–E) is taken from ref. 6, eqn. (10), Table V, and is:

$$\mathcal{H} = DQ|A_{1g}O(i)|^{4}_{O_h} + DS|E_gO(\theta)|^{2}_{O_h} + DT|E_gO(\theta)|^{4}_{O_h}$$

The matrix elements for the d^7 (cobalt (II)) and d^8 (nickel(II)) wavefunctions are also presented in ref. 6 (use Table X with the coefficients of DQ, DS and DT multiplied by -1 for the d^8 case). First, consider the electronic spectrum of $Ni(LL)_2Br_2$ shown in Fig. 2. The initial imperative is to assign the transitions according to the scheme in Fig. 1.

Often such assignment is straightforward without the need to undertake a single-crystal polarized light study to confirm the assignment unequivocally.

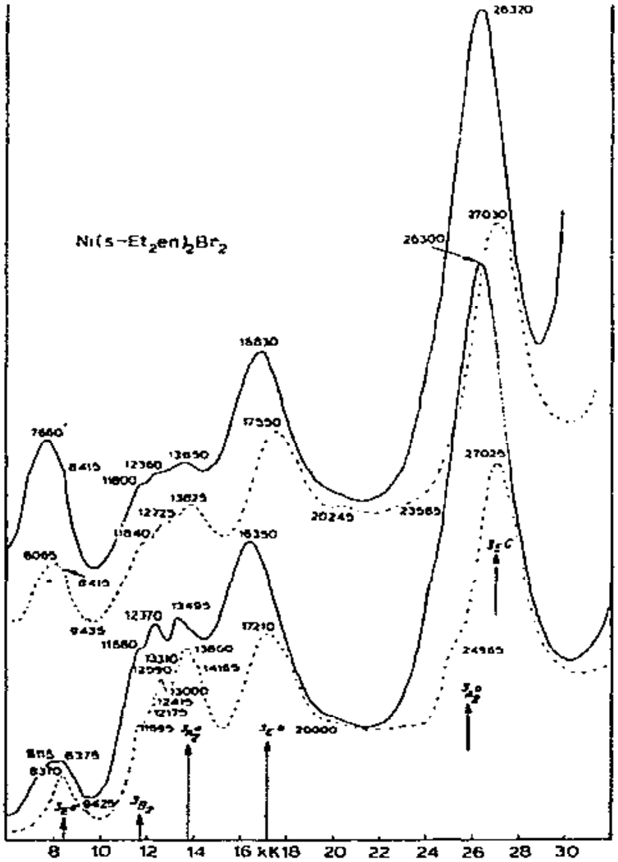

Fig. 2. Single crystal electronic spectrum at ca. 10 K of $Ni(s\text{-}Et_2en)_2Br_2$. Two polarizations are displayed. Solid lines, room temperature; hatched lines, 10 K. Adapted from ref. 11.

TABLE 1

Splitting sense of orbital triplets in D_{4h} symmetry[a]

d^2, d^7	d^3, d^8	Criterion
$B_2(T_2)$–$E^b(T_2)$	$E^a(T_2)$–$B_2(T_2)$	$DQ_A - DQ_E$
—	$E^b(T_1(F))$–$A_2^a(T_1(F))$	$-(2d\sigma+2d\pi)$
$A_2^a(T_1(F))$–$E^a(T_1(F))$	—	$d\pi$[b]
$A_2^b(T_1(P))$–$E^c(T_1(P))$	$E^c(T_1(P))$–$A_2^b(T_1(P))$	$(-2d\pi)$
$B_1(A_2)$–$B_2(T_2)$	$B_2(T_2)$–$B_1(A_2)$	$10Dq\,[DQ_E/6\sqrt{21}\,]$[c]

[a] Transition to the left component of each state is at an energy higher than to the right when the value of the function in column 3 is positive, and vice versa. Excludes configurational interaction except where indicated.

[b] Includes configurational interaction but there is also a small dependence on $d\sigma$.

[c] Transition energy separation exactly equal to $10\,Dq$, inclusive of configurational interaction. Transitions to E states are generally more intense than transitions to singly degenerate states.

Table 1 summarizes the conditions which dictate the sense of the splitting of the various T (in O_h) terms under a D_{4h} distortion. Note that most of these are first-order conditions (excluding configurational interaction). If the splitting of the T term is large, they are likely to be useful; if the splitting is small they should be used with caution. For example, the splitting of the ground term ($T_{1g}(F)$) in D_{4h} d^2 and d^7 is much smaller than the first-order analysis suggests and is primarily dependent upon the sign of $d\pi$ [6,10].

For the nickel complex, and assuming for the moment that the complex possesses microstoichiometry A, C, D or E, the assignment indicated in Fig. 2 follows automatically from the considerations in Table 1. There is little ambiguity in this case, though this will not necessarily always be true.

Using the appropriate F term matrices (Table X, ref. 6) the DQ, DS, DT and B values which reproduce this spectrum (Fig. 2) can be derived (see Table 2) [11]. We note an alternative procedure for solving these spectra, introduced for d^8 ions by Bartecki and Kurzak [12]. This procedure, whilst conveniently usable with only a hand calculator or similar instrument, requires knowledge of all six transitions and should be used with caution. It is discussed in the Appendix to this article.

Under normal circumstances we do not know the structure of the nickel complex and may consider that it could possess structures A, *trans*-[M(LL)$_4$Br$_2$]; B, *cis*-[M(LL)$_2$Br$_2$]; C or D, [M(LL)$_4$Br$^+$Br$^-$]; or E, [M(LL)$_4^{2+}$ 2 Br$^-$ (high spin)], where, with the exception of D, all angles are supposed to be close to 90°.

A mapping of the NSH and AOM parameters (eqns. (1)–(28) below) is

TABLE 2

$Ni(s\text{-}Et_2en)_2Br_2 \equiv Ni(LL)_2Br_2$

	$Ni(LL)_2Br_2$ $A\text{-}D_{4h}$ [a]	$Ni(LL)_2Br^+ Br^-$ $C\text{-}C_{4v}$ [a]	$Ni(LL)_2Br_2$-*cis* $B\text{-}C_{2v}$ [b]
σ_N	3923	3923	4120
σ_{Br}	1178	2356	4211
π_{Br}	−644	−1288	2142
$d\sigma$	−2058	−1175	68
$d\pi$	−644	−1288	−1071

[a] Assignment as shown in Fig. 2. $DQ = 27171$; $DS = -6777$; $DT = -4383$; $B = 845$; $DQ_A = 16799$; $DQ_E = 32357$; good fit.

[b] Inverted assignment appropriate to *cis* configuration (but with $E(T_1(P)) > A_2(T_1(P))$. $DQ = 26385$; $DS = -2233$; $DT = 3213$; $B = 901$; $DQ_A = 33988$; $DQ_E = 22583$; poor fit. All data in wavenumbers.

TABLE 3

One electron matrix elements within the AOM and NSH formalisms. NSH: the following matrix elements are appropriate for D_{4h}, C_{4v} and C_{2v} (intermediate symmetry D_{4h}) and to the D_{2h} example. Note that DU and DV are zero in all cases except D_{2h} [43].

$z^2|\hat{O}|z^2\rangle = (1/\sqrt{21})DQ + (2/7)DS + (5/7\sqrt{15})DT$

$xz|\hat{O}|xz\rangle = -(2/3\sqrt{21})DQ + (1/7)DS - (10/21\sqrt{15})DT + (\sqrt{3}/7)DU + (10/21\sqrt{5})DV$

$yz|\hat{O}|yz\rangle = -(2/3\sqrt{21})DQ + (1/7)DS - (10/21\sqrt{15})DT - (\sqrt{3}/7)DU - (10/21\sqrt{5})DV$

$xy|\hat{O}|xy\rangle = -(2/3\sqrt{21})DQ - (2/7)DS + (20/21\sqrt{15})DT$

$x^2-y^2|\hat{O}|x^2-y^2\rangle = (1/\sqrt{21})DQ - (2/7)DS - (5/7\sqrt{15})DT$

$x^2-y^2|\hat{O}|z^2\rangle = -(2/7)DU + (5/7\sqrt{15})DV$

OM

$_{4h}$ ML_4Z_2 (Z on z axis)		C_{4v} ML_4Z (Z along z axis, general solution) in-plane $\theta = 90°$	
$z^2\|\hat{O}\|z^2\rangle$	$= 2\sigma_Z + \sigma_L$	$\langle z^2\|\hat{O}\|z^2\rangle$	$= (1/4)(1+3\cos 2\theta)^2\sigma_L + (3\sin^2 2\theta)\pi_L + \sigma_Z$
$xz\|\hat{O}\|xz\rangle$	$= 2\pi_L + 2\pi_Z$	$\langle xz\|\hat{O}\|xz\rangle$	$= (1.5\sin^2 2\theta)\sigma_L + 2(\cos^2\theta + \cos^2 2\theta)\pi_L + \pi_Z$
$yz\|\hat{O}\|yz\rangle$	$= 2\pi_L + 2\pi_Z$	$\langle yz\|\hat{O}\|yz\rangle$	$= (1.5\sin^2 2\theta)\sigma_L + 2(\cos^2\theta + \cos^2 2\theta)\pi_L + \pi_Z$
$xy\|\hat{O}\|xy\rangle$	$= 4\pi_L$	$\langle xy\|\hat{O}\|xy\rangle$	$= 4\pi_L$
$x^2-y^2\|\hat{O}\|x^2-y^2\rangle$	$= 3\sigma_L$	$\langle x^2-y^2\|\hat{O}\|x^2-y^2\rangle$	$= (3/4)(1-\cos 2\theta)^2\sigma_L + (\sin^2 2\theta)\pi_L$

is-ML_4Z_2 C_{2v} (x, y, z passing through ligands)		$MX_2Y_2Z_2$	D_{2h}
$z^2\|\hat{O}\|z^2\rangle$	$= 2.5\sigma_L + 0.5\sigma_Z$	$\langle z^2\|\hat{O}\|z^2\rangle$	$2\sigma_z + \frac{1}{2}(\sigma_x + \sigma_y)$
$xz\|\hat{O}\|xz\rangle$	$= 3\pi_L + \pi_Z$	$\langle xz\|\hat{O}\|xz\rangle$	$2\pi_x + 2\pi_z$
$yz\|\hat{O}\|yz\rangle$	$= 3\pi_L + \pi_Z$	$\langle yz\|\hat{O}\|yz\rangle$	$2\pi_y + 2\pi_z$
$xy\|\hat{O}\|xy\rangle$	$= 2\pi_L + 2\pi_Z$	$\langle xy\|\hat{O}\|xy\rangle$	$2\pi_x + 2\pi_y$
$x^2-y^2\|\hat{O}\|x^2-y^2\rangle$	$= 3/2(\sigma_z + \sigma_L)$	$\langle x^2-y^2\|\hat{O}\|x^2-y^2\rangle$	$3/2(\sigma_x + \sigma_y)$
		$\langle x^2-y^2\|\hat{O}\|z^2\rangle$	$(\sqrt{3}/2)(\sigma_y - \sigma_x)$

obtained using the data presented for the one electron *d* orbital energies for each configuration in Table 3, by equating energy differences between pairs of orbitals, in the two models. The mapping is, in general, independent of the metal ion.

In all examples, the NSH and classical approaches [13] are linked through the expressions

$$DQ = 6(\sqrt{21})\, Dq - 3.5\sqrt{21}\, Dt \tag{1}$$

$$DS = -7Ds \tag{2}$$

$$DT = -3.5\sqrt{15}\, Dt \tag{3}$$

The sign of Dt, variable in the literature is defined via

$$Dt = (4/7)(Dq_e - Dq_a) \tag{4}$$

where Dq_e is the classical equatorial field strength, and Dq_a is the classical axial field strength.

The corresponding NSH parameters are DQ_E (equatorial field strength) and DQ_A (axial field strength) defined by

$$DQ_E = DQ - (\sqrt{7}/\sqrt{5})DT \tag{5}$$

$$DQ_A = DQ + 2(\sqrt{7}/\sqrt{5})DT \tag{6}$$

and the global DQ value, defining the totally symmetric (A_{1g}) component of the field is linked thereto via

$$DQ = (1/6)(4DQ_E + 2DQ_A) \tag{7}$$

There follows the relationships connecting the AOM and NSH models for the various configurations.

(1) A. trans-ML_4Z_2

$$DQ = (\sqrt{21}/5)[3\sigma_Z + 6\sigma_L - (4\pi_Z + 8\pi_L)] \tag{8}$$

$$DS = 2(\sigma_Z + \pi_Z - \sigma_L - \pi_L) \tag{9}$$

$$DT = (\sqrt{15}/5)[(3\sigma_Z - 4\pi_Z - 3\sigma_L + 4\pi_L)] \tag{10}$$

$$\sigma_N = (5/9)((1/\sqrt{21})DQ - (1/\sqrt{15})DT) \tag{11}$$

$$\sigma_Z = ((1/189)(5\sqrt{21}\,DQ + 54DS + 2\sqrt{15}\,DT)) \tag{12}$$

$$d\pi = (3/14)DS - (1/7)(\sqrt{5/3})DT \tag{13}$$

$$d\sigma = (1/28)[6DS + \sqrt{15}\,DT] \tag{14}$$

These equations are also appropriate for the high-spin square planar possibility E (rarely if ever observed) when the axial AOM parameters approach zero. The possibility of d–s mixing occurs in this case, and should be considered [2].

(2) C square pyramidal $ML_4Z^+Z^-$ (metal in plane)

$$DQ = \sqrt{21}\,[1.2\sigma_L + 0.3\sigma_Z - 0.4d\pi] \tag{15}$$

$$DS = d\pi + \sigma_Z - 2\sigma_L \tag{16}$$

$$DT = (3\sqrt{15}/10)[\sigma_Z - 2\sigma_L - (4/3)d\pi] \tag{17}$$

$$\sigma_L = (5/9)\{(DQ/\sqrt{21}) - (DT/\sqrt{15})\} \tag{18}$$

$$\sigma_Z = (10/9\sqrt{21})DQ + (20/63\sqrt{15})DT + (4/7)DS \tag{19}$$

$$d\pi = (1/7)[3DS - (10/\sqrt{15})DT] \tag{20}$$

$$d\sigma = 0.75[(5/9\sqrt{21})DQ + (55/63\sqrt{15})DT + (4/7)DS] \tag{21}$$

(3) D square pyramidal $ML_4Z^+Z^-$ (metal out-of-plane)

The matrix elements for this case are included in Table 3. It is readily seen that if the metal is a few tenths of an Angström above the molecular (xy) plane, the angle θ typically increases only about 6–8°. This introduces only a small perturbation in the d orbital AOM energies, and is not further considered here.

With the assignment shown in Fig. 2, based upon Table 1, and appropriate for A, C, D or E, we generate the AOM parameters shown in Table 2.

The AOM parameters, axial and equatorial field strengths are all acceptable for the *trans*-M(LL)$_2$Br$_2$ formulation A when compared with the anticipated values derived from the previous literature (see Section B). Thus the electronic spectrum is consistent with formulation A. Formulation C, square pyramidal, results in AOM parameters for the single bromide ion significantly above the anticipated value. Thus the spectra are inconsistent with the formulations C or D. Similarly the presence of a strong axial field mitigates against the square-planar formulation E.

It remains to consider a *cis* configuration B (all angles 90°). Here the intermediate symmetry allows one to consider that the plane is composed of the summation of amine nitrogen plus bromide along the x and y coordinates, with two amine nitrogen atoms along the z axis. Therefore, the axial field for this molecule should be similar to the equatorial field in a truly *trans* N$_4$ example. Since the intermediate symmetry is effectively D_{4h}, the same Hamiltonian, (1) may be employed.

The relationship between NSH and AOM parameters is now given.

(4) B cis-ML_4Z_2 C_{2v} *(Intermediate symmetry* D_{4h}*) (90° angles)*

$$DQ = (\sqrt{21}/5)[6\sigma_L + 3\sigma_Z - (4\pi_Z + 8\pi_L)] \tag{22}$$

$$DS = \sigma_L - \sigma_Z - \pi_Z + \pi_L \tag{23}$$

$$DT = (\sqrt{15}/10)[3\sigma_L - 3\sigma_Z + 4(\pi_Z - \pi_L)] \tag{24}$$

$$\sigma_L = (5/9\sqrt{21})DQ + (10/9\sqrt{15})DT \tag{25}$$

$$\sigma_Z = (5/9\sqrt{21})DQ - (20/63\sqrt{15})DT - (4/7)DS \tag{26}$$

$$d\pi = (-3/7)DS + (10/7\sqrt{15})DT = \pi_Z - \pi_L \tag{27}$$

$$d\sigma = (0.75)[-(4/7)DS - (10/7\sqrt{15})DT] = 0.75(\sigma_Z - \sigma_L) \tag{28}$$

If the same assignment is used, the σ parameter for bromide is over 7000 cm^{-1}, clearly unacceptable. However, it is inappropriate to use the same assignment. In the *cis* case, with bromide accepted as a weaker σ donor than amine nitrogen, the McClure parameter $d\sigma$ is now positive, and the axial field is stronger than the equatorial field. Using Table 1, the lower two orbital triplets, in octahedral symmetry, are expected to split in the opposite sense, compared to that seen previously. If this revised assignment is used the NSH and AOM parameters shown in Table 2 are obtained. The fit of the observed to calculated energies is very poor, and the AOM parameters for the bromide ion are not acceptable. Thus the *cis* configuration B seems eliminated. The data are, therefore, fully consistent with formulation A which is believed to be correct based on the accumulated IR and electronic spectra, and magnetism [14]. We have chosen in this treatment to ignore the bidentate nature of the amine ligands. Such consideration would have the effect of reducing the symmetry to a twofold group, at best. However, such rhombic distortion does not show up at the level of analysis discussed here. It can be recognized via comparison of the variously polarized spectra [11], (but see cobalt(II) data below). The possibility of angular distortion will be explored below.

The spectrum of the cobalt(II) analog, $Co(LL)_2Br_2$ is shown in Fig. 3. Well-defined splitting of the various orbital triplet states (in O_h symmetry) is observed. Using the guides in Table 1 the assignment shown in Fig. 3 is derived. The splitting of the ground state ($T_{1g}(F)$ in O_h) is expected to be small and it is not immediately apparent which states, ${}^4A_{2g}$ or ${}^4E_g$ will be the ground state in D_{4h} symmetry. When configurational interaction is taken into account, the splitting of the $T_{1g}(F)$ level is primarily defined by $d\pi$, positive $d\pi$ yielding an ${}^4E_g$ ground term, and negative $d\pi$ a ${}^4A_{2g}$ ground term [6,10]. However, in cobalt(II) chemistry, $d\pi$ is a sufficiently small parameter that it cannot be safely predicted. Both ground state possibilities must be consid-

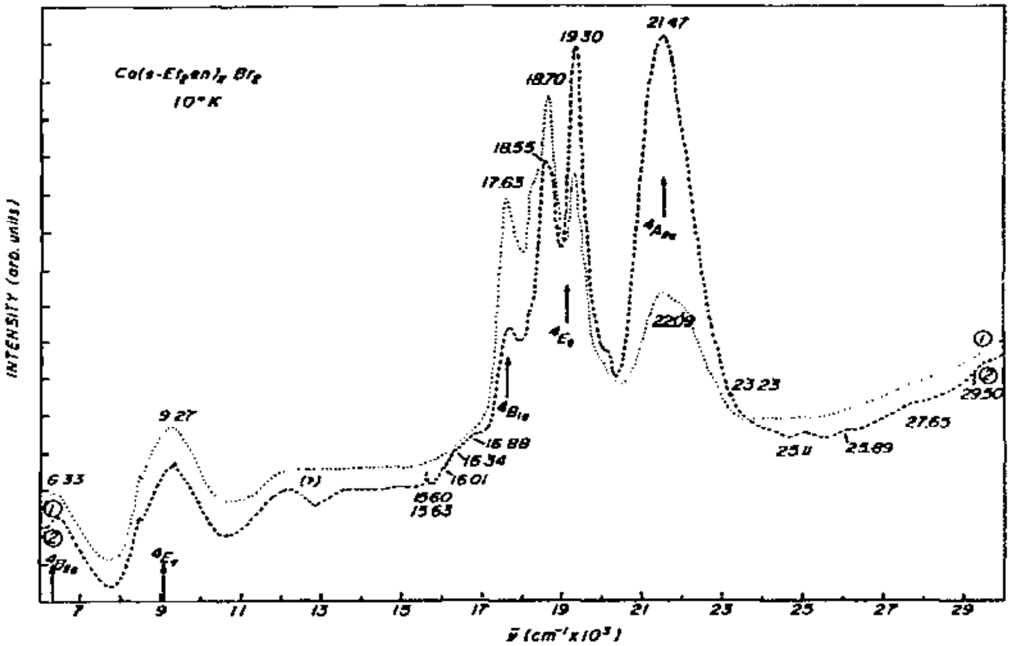

Fig. 3. Single crystal electronic spectrum at ca. 10 K of Co(s-Et$_2$en)$_2$Br$_2$. Two polarizations are displayed. Solid lines, room temperature; hatched lines, 10 K. Adapted from ref. 10.

ered. The same Hamiltonian and matrices (the d^2 matrices in Table X of ref. 6) may be used for cobalt(II) as previously used for nickel(II) (also see Appendix). The iterative programme to fit the spectra should be written to consider both ground state possibilities.

TABLE 4

Co(s-Et$_2$en)$_2$Br$_2$ = Co(LL)$_2$Br$_2$

	Co(LL)$_2$Br$_2$ A–D_{4h} [a]	Co(LL)$_2$Br$^+$ Br$^-$ C–C_{4v} [a]	*cis*-Co(LL)$_2$Br$_2$ B–C_{2v} [b]
σ_N	3768	3768	3850
σ_{Br}	1938	3876	1235
π_{Br}	144	289	−365
$d\sigma$	−1372	82	−1961
$d\pi$	144	289	182

[a] Assignment as shown in Fig. 2. $DQ = 25518$; $DS = -3370$; $DT = -4699$; $B = 847$; $DQ_E = 31078$; $DQ_A = 14398$; $Dq = 1130$ cm; good fit.

[b] Inverted assignment. $DQ = 25912$; $DS = 2980$; $DT = 2473$; $B = 888$; $DQ_E = 31764$; $DQ_A = 22986$ cm^{-1}; poor fit. All data in wavenumbers.

Table 4 contains the NSH and AOM parameters for this complex assuming formulations A, C, D or E, and eqns. (1)–(21). Once again only formulation A, *trans*-Co(LL)$_2$Br$_2$ provides a fully acceptable data set. In this case the *cis*-(B) data set, obtained by inverting the order of the splitting of the T states, relative to the *trans* example (Fig. 3) appears not unreasonable. However, the fit of experimental to calculated band energy is poor, with one band deviating by about 1500 cm^{-1}.

The cobalt(II) assignments are not so clearcut as those of nickel(II). The presence of quartet–doublet transitions, and the absence of a large data base of previously described compounds requires that these data be treated with caution. For example, the assignments of the 17.63 and 19.00 kK bands could be interchanged. This would yield a rather higher value for DQ_e in the *trans* case than seems likely.

Note also that the $^4E_g(P)$ term is apparently split in this bromide complex. This may arise as a consequence of the bidentate nature of the diamine (highest real symmetry D_{2h}) or of crystal packing. We have used an average value for these calculations.

A bad fit to the matrices may be considered evidence of an incorrect assignment, provided that the molecule does indeed belong, to a good approximation, to the point group used to generate the matrices. A good fit does not in itself guarantee a correct assignment.

The species Ni(LL)$_2$(maleate) [15a] is believed to have a *cis* configuration, B, through bidentate binding of the maleate group, and will exhibit intermediate D_{4h} symmetry. Its solution spectrum is reproduced in Fig. 4.

The transition to $^3B_2$ should now lie below that to $^3E_g^a$. The former

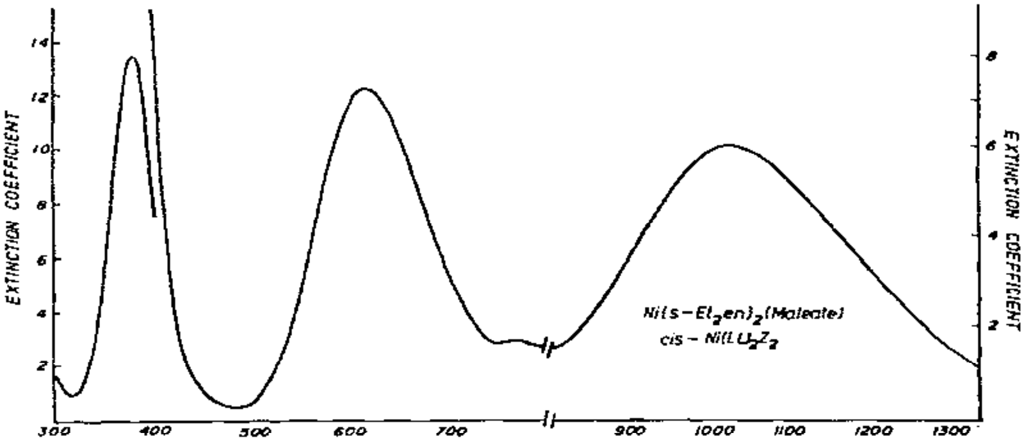

Fig. 4. Room temperature solution (dichloromethane) electronic spectrum of Ni(s-Et$_2$en)$_2$maleate.

transition has an energy proportional to the equatorial field of the amine nitrogen plus maleate carboxylate ligands. If the AOM values pertinent to a *trans* complex [16] are used to derive the transition energies, the splitting of the orbital triplets is quite small as anticipated from previous studies with chromium(III) and cobalt(III) [5]. Indeed, as is evident, the spectrum appears octahedral (Fig. 4). Although the spectroscopic resolution is too small, in this case, to derive any useful bonding parameters, it is clear that the complex is *cis*, since splitting would certainly be observed, even at room temperature, if a *trans* structure were present.

(b) $MX_2Y_2Z_2$ complexes

If X is *trans* to the different ligand Y then we have the situation as described above for the *cis* complexes, intermediate D_{4h} symmetry being involved. If X is *trans* to X, such complexes have D_{2h} symmetry, at best, intermediate symmetry not being invokable. We have recently investigated the complex Ni(asym-dimethylethylenediamine)$_2$(trichloroacetate)$_2$, Ni(LL′)$_2$(TCA)$_2$, having such symmetry (Fig. 5) [18].

The Hamiltonian must now possess two additional terms, namely

$$\mathcal{H} = DQ|A_{1g}O(i)|^4_{O_h} + DS|E_gO(\theta)|^2_{O_h} + DT|E_gO(\theta)|^4_{O_h}$$
$$+ DU|E_g2+(\epsilon)|^2_{O_h} + DV|E_g2+(\epsilon)|^4_{O_h}$$

The complete mapping between NSH and AOM is provided by

$$DQ = (\sqrt{21}/5)[3(\sigma_x+\sigma_y+\sigma_z) - 4(\pi_x+\pi_y+\pi_z)] \qquad (29)$$

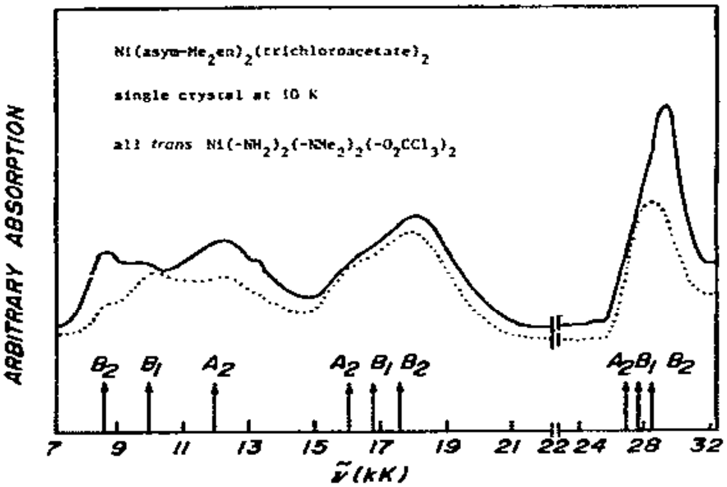

Fig. 5. Single crystal electronic spectrum at ca. 10 K of Ni(as-Me$_2$en)$_2$(trichloroacetate)$_2$. Two different 10 K polarizations are shown. Adapted from ref. 17.

$$DS = (2\sigma_z + 2\pi_z) - (\sigma_x + \pi_x) - (\sigma_y + \pi_y) \tag{30}$$

$$DT = (\sqrt{15}/5)[3\sigma_z - 1.5(\sigma_x + \sigma_y) - 4\pi_z + 2(\pi_x + \pi_y)] \tag{31}$$

$$DU = \sqrt{3}(\pi_x - \pi_y) - \sqrt{3}(\sigma_y - \sigma_x) \tag{32}$$

$$DV = (6/\sqrt{5})[(\pi_x - \pi_y) + (3/4)(\sigma_y - \sigma_x)] \tag{33}$$

$$\begin{aligned}\sigma_z = (1/9)\big[&(5/\sqrt{21})DQ + (18/7)DS + (10/7\sqrt{15})DT \\ &+ (6\sqrt{3}/7)DU + (20/7\sqrt{5})DV + 12\pi_y\big]\end{aligned} \tag{34}$$

$$\sigma_y = \sigma_z - (2/7)DS - (5/7\sqrt{15})DT - (2/7\sqrt{3})DU + (\sqrt{5}/21)DV \tag{35}$$

$$\sigma_x = 2\sigma_z - \sigma_y - (4/7)DS - (10/7\sqrt{15})DT \tag{36}$$

$$\pi_z = (3/14)DS - (5/7\sqrt{15})DT + (\sqrt{3}/14)DU + (5/21\sqrt{5})DV + \pi_y \tag{37}$$

$$\pi_y = 0 \text{ (assumed)} \tag{38}$$

$$\pi_x = (\sqrt{3}/7)DU + (10/21\sqrt{5})DV + \pi_y \tag{39}$$

There is insufficient information in the spectrum to solve unequivocally for all these parameters. However, the usual assumption of zero π bonding by the diamine eliminates π_N (π_x and π_y above) and reduces the AOM data set to four.

The spectrum can now be solved. Note that *DU* and *DV* are not linearly independent but are related by the difference in the σ bonding along the *x* and *y* axes. Note also that the lowest orbital triplet has clearly split into three components, but that the upper triplets do not appear very different from the analogous D_{4h} complex containing the symmetric diamine [16]. It is well known that distortion is more evident in the lower orbital triplet than in higher orbital triplets [5,13]. This problem was solved by initially trying the AOM parameters used for the complex Ni(sym-dimethylethylenediamine)$_2$-(trichloroacetate)$_2$ and iterating a solution using ($\sigma_N(NH_2) - \sigma_{N'}(NMe_2)$) as a variable. Small modification of the initial input AOM parameters gave the solution graphed in Fig. 6. Agreement between observed and calculated spectra is most satisfactory.

There is no doubt that the nickel–N(Me)$_2$ bond is about 8 pm longer than the Ni–NH$_2$ bond in this molecule [17]. A fit is achieved at a value of $\sigma_N - \sigma_{N'} = 1025\ \text{cm}^{-1}$, leading to the data set

$$\sigma_N = 4700;\ \sigma_{N'} = 3675;\ \sigma_O = 2800;\ \pi_O = 460\ \text{cm}^{-1}\left[\pi_{NMe_2} = 120\ \text{cm}^{-1}\right]$$

which is usefully compared with the symmetric diamine trichloroacetate having

$$\sigma_N = 4100;\ \sigma_O = 2425;\ \pi_O = -215\ \text{cm}^{-1}$$

The difference in sign in the π_O parameter has no significance in view of its small absolute value. In general the π parameter is poorly defined and in nickel(II) and cobalt(II) complexes, at least, normally has such a small relative value that π bonding can generally be ignored.

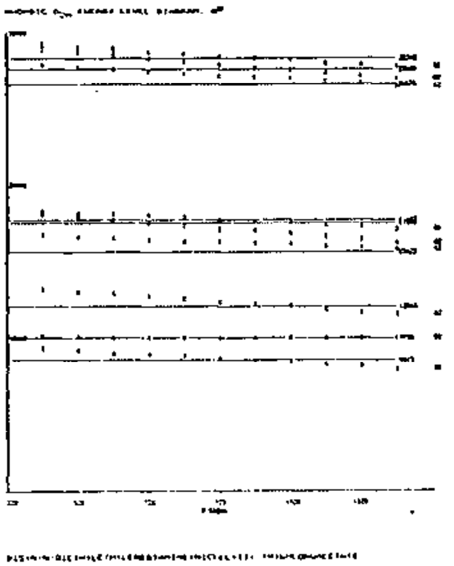

Fig. 6. Energy levels in D_{2h} symmetry as a function of $d\sigma(N,N')$. The parameters $\sigma_N=4400$, $\sigma_O=2800$, $\pi_O=400$ and $B=875$ cm^{-1} are assumed. Reproduced with permission from ref. 16.

General chemical experience leads one to expect that if one bond is weakened, others will strengthen to accomodate the extra positive charge left on the metal. In comparing these data we note a definite increase in the σ_N and σ_O when a pair of *trans* N′ ligands are weakened. The positive change in π_O may also be significant though it is not too useful to argue about such relatively small numbers.

(1) Angular distortion

The inclusion of angular distortion, where known, into the AOM matrices [7,8] presents no problem and has been discussed by others [18]. Essentially all studies to date, however, have involved ligands which could be assumed to be axially symmetric such that each M–L interaction could be described by $C_{\infty v}$ symmetry. Recently, we have studied bidentate nitrite complexes of the type $Ni(LL)_2(ONO)^+NO_2^-$ which parallel the *cis* complexes discussed above, B, but which have the added complexity that the metal nitrite angles are not 90° and the bidentate nitrite can only dubiously be regarded as axially symmetric. A typical spectrum is shown in Fig. 7 together with the calculated band energies. Since the analysis of these complexes does not have

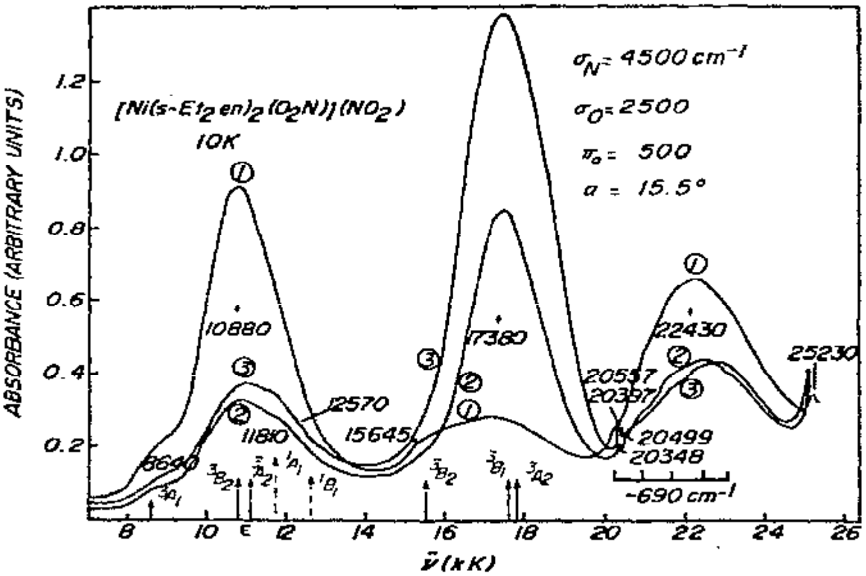

Fig. 7. Single crystal electronic spectrum, at ca. 10 K of $[Ni(s\text{-}Et_2en)_2O_2N]^+ NO_2^-$. Three polarizations are displayed. Parameters and assignments as indicated.

general utility (each distorted complex must be considered separately) we do not repeat the argument here, but refer the reader to the original paper [15]. It is important to note, however, that the AOM parameters which fit this spectrum (Fig. 7) are very similar to those used to fit analogous *trans* complexes. Evidently, for these relatively ionic six coordinate complexes, the transferability of parameters is fairly good.

We have used, in this section, examples chosen from our own work: however, important work is emanating from many laboratories. We refer the reader especially to contributions by Schäffer, Gerloch, Gatteschi, Bertini, Hitchman, Horrocks and their respective co-workers. Some of this work is referenced below.

C. ORBITAL ANGULAR OVERLAP MODEL (AOM) PARAMETERS

We present in Tables 5–8 representative data for a range of neutral and anionic ligands bound to chromium(III), cobalt(II) and nickel(II). Most of these data are obtained from analysis of tetragonal complexes. When π bonding can be assumed to be zero (e.g. saturated amine ligands), parameters can be derived from octahedral complexes by dividing $10Dq$ by 3 ($10Dq = 3\sigma - 4\pi$).

TABLE 5

Chromium(III). σ parameter ranges for neutral and anionic ligands (data in cm^{-1})

Ligand	Range	Ref.	Ligand	Range	Ref.
NH_3	6970–7265	20, 21	F^-	7400–9095	20–22
$R-NH_2$	6640–7835	20, 21	Cl^-	5465–5860	20–22
DMSO	6770	21	Br^-	4800–5420	20–22
Py	5800	22	I^-	3985–4290	21
H_2O	6765–7900	20–22	OH^-	7475–8670	20–22

$R-NH_2$ covers several organic primary amines.
Data rounded off to the nearest 5 cm^{-1}.

Recently, some data have been derived from the spectra of substituted tetrahedral complexes [25–28] of C_{2v} or D_{2d} symmetry. Some of these parameters, especially where halide ions are concerned are substantially higher than those derived from tetragonal spectra. Where nitrogen ligands are concerned, the parameters for both stereochemistries are similar. Insufficient data are available to decide whether the increase in the magnitude of the AOM parameters for the halogens in the tetrahedral complexes is real. Increased covalency with these polarizable ligands, in the tetrahedral complexes, may be an important factor.

Pyridine N-oxide and its substituted derivatives form both octahedral and trigonal bipyramidal complexes with cobalt(II). The AOM σ and π parameters for the M–O bond appear significantly larger in the five-coordinate than in the six-coordinate complex [30,33] (Table 7).

AOM data may be obtained from analysis of single crystal magnetic or

TABLE 6

Chromium(III). π parameter ranges for neutral and anionic ligands (data in cm^{-1})

Ligand	Range	Ref.	Ligand	Range	Ref.
NH_3	0		F^-	1620–2045	20–22
$R-NH_2$	0	20, 21	Cl^-	870–1050	20–22
DMSO	1655	21	Br^-	625– 905	20–22
Py	−500	22	I^-	595– 740	21
H_2O	750–1925	20–22	OH^-	1405–2250	20–22

$R-NH_2$ covers several organic primary amines.
Data rounded off to the nearest 5 cm^{-1}.

TABLE 7

High spin cobalt(II). σ parameter ranges for neutral and anionic ligands (data in cm^{-1})

Ligand	Range	Ref.	Ligand	Range	Ref.
H_2O	3635	34	NCS^-	3700–4045	10, 29
NH_3	3400 [a,b]	5	Cl^- [c]	2300–3000	10, 29, 31
–NHEt	3765–4065	10	Br^- [c]	1940	10
Py	3700	31			
PyO	4300	30	$AcAc^-$	4500–4580	34
PyO	4725, 5250 [d]	33			
MQuin	3910 [e]	34			

$R-NH_2$ covers several organic primary amines.

Data rounded off to the nearest 5 cm^{-1}.

[a] Assumes $\pi = 0$.

[b] Tetrahedral values range from 3000 cm^{-1} for Br^- to as high as 4700 cm^{-1} for Cl^- depending upon approximation.

[c] Octahedral complex.

[d] $Co(PicNO)_5^{++}$, axial and equatorial σ values, respectively. The $\pi(ax) = 1185$ cm^{-1} and $\pi(eq) = 1315$ cm^{-1}.

[e] $\pi = 675, 785$ cm^{-1}; AcAc = M–O in acetylacetone, MQuin = 6-methylquinoline.

The π parameters are generally very small and except in the footnotes, are not tabulated. For an extensive, but approximate, listing of AOM parameters for a wide range of low symmetry cobalt (and nickel) complexes, see ref. 24.

ESR data as shown recently by, for example, the groups of Gatteschi and of Gerloch [18,25–27,33,35]. The parameters may be less accurately defined especially where static magnetic susceptibility is concerned. Sometimes the numerical values obtained are grossly different from those previously identified in electronic spectroscopic analysis. In other cases, the same set of parameters can be used to explain both the magnetic and spectroscopic results. Whilst this latter agreement sounds admirable, it is not, in fact, obvious, that the same set of parameters should satisfy data for both experiments. In the magnetic experiments we are probing ground-state properties, whilst in the spectroscopy we are probing excited-state energies, albeit Franck–Condon in nature. Moreover, the inclusion of vibronic contributions to excited-state transition energies can significantly perturb the numerical magnitudes so obtained.

The data shown in Tables 5–8 mask synergistic and stereochemical phenomena namely (a) the presence of one M–L bond in a molecule can modify the magnitude of the parameters in another M–L′ bond, and (b) the magnitudes of the parameters may be stereochemistry dependent, as alluded to above.

TABLE 8

Nickel(II). σ parameter ranges for neutral and anionic ligands (data in cm^{-1})

Ligand	Range	Ref.	Ligand	Range	Ref.
H_2O	1760–2200	11	NCS^-	3830–3950	11, 31
NH_3	3585–3600	5, 31	Cl^-	1710	11
$-NHMe$	4000–4200	11, 16	Br^-	1180	11
$-NHEt$	3925–4350	11, 16, 17	NO_3^-	1065	11
$-NMe_2$	3700	17	TCA^-	2350–2800	16, 17
$-NEt_2$	~2400	15a,b	DCA^-	2410–2430	16
Quin	3500–4500 [a]	25			
Py	4500–4630 [b]	19, 32			
PyO	4395 [c]	23			
$-P$ [d]	5000–6000 [a]	25			

$R-NH_2$ covers several organic primary amines.

Data rounded off to the nearest 5 cm^{-1}.

Quin = quinoline, Py = pyridine, PyO = pyridine *N*-oxide, TCA = trichloroacetate, DCA = dichloroacetate.

[a] Substituted tetrahedral.

[b] π_N 500–570 cm^{-1}.

[c] Two orthogonal π_O values of 830 and 1660 cm^{-1}.

[d] A range of tetrahedral phosphine derivatives, $\pi_P = -1500$ cm^{-1}.

A selection of values for different amines may be obtained from ref. 5, Table 9.23 by dividing 10*Dq* by 3.

Earlier in this article we demonstrated the effect of a weak interaction along one axis (long bond) causing a tightening up (increase in parameter values) along other axes. This is a quite general phenomenon well documented in chemistry [36], and certainly not unexpected.

In discussing tetragonal complexes a number of authors have demonstrated an increase in equatorial field strength as the axial field decreases [36–41], and vice versa. It is probable that both electronic and steric effects are involved. Steric effects certainly play an important role in tetragonal cobalt and nickel complexes of sym-*N*,*N′*-diethylethylenediamine, for example, where the axial field strengths of halide and water are invariably lower than in octahedral analogs [5,10,11]. Where ethylenediamine complexes of chromium are concerned, this steric effect seems almost absent, the field strengths derived from the tetragonal complex being much more closely similar to normal octahedral values.

The data discussed so far refer to high-spin derivatives. Low-spin data, for example, square-planar nickel(II) and cobalt(II) exist in the literature but the uncertainties in these data make it premature to review them here. Since the bond lengths are generally shorter in low-spin systems, higher magnitude AOM parameters are expected and are certainly observed. Thus spin state will influence parameter values.

Clearly all of these factors must be considered when assessing whether an AOM parameter is "reasonable" or not. More crucially the AOM model apparently provides a mechanism to detect such variations in bonding from one complex to another. The transferability argument should be used with care, lest the chemistry be lost! Finally, we note that the AOM model reflects the anti-bonding energies of the *d* orbitals. The parameters may tacitly be assumed to reflect the M–L bonding energies. However, such an assumption must be treated with caution [42].

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APPENDIX

Recently, Bartecki and Kurzak [12] have published linear solutions to the tetragonal d^8 matrices providing values of Ds and Dt as a function of all six observable tetragonal transitions, $\nu1$–$\nu6$. Since there are several typographical errors in their paper, we repeat these equations here. We also extend them to d^7. Indeed the equations reproduced here can be used for d^2, d^3, d^7 and d^8 tetragonal systems.

However, there is clearly redundancy in that six observables are used to compute three parameters. These authors primarily used the invariance of the trace of a matrix to solve the matrix equations. If all six transitions are observed, and if there is a perfect fit to the matrices, then these equations yield the same parameters as a least-squares iterative program would provide. If only five observables are seen, a simple program can be written to iterate over the sixth. However, it is imperative to compare the calculated individual transition energies generated by the resulting parameter set with the observed transition energies. If the experimental data set used does not fit the matrix equations perfectly, as will generally be the case, then this procedure does not usually give such a good fit as an iterative least-squares program would provide. The fit to each of the sums of the A_2 and E transition energies will be exact, but the fit to individual energies may be poor. The procedure is capable of being programmed into a programmable calculator (or microcomputer) and is attractive for this reason. It must, however, be used with care.

Unlike the previous authors a specific labelling is chosen here for six transitions irrespective of their energy order, reducing the complexity of the approach as previously published [12].

(a) d^3 and d^8 $A_{2g}(F)$ ground term in O_h and $B_{1g}(F)$ ground term in D_{4h}.

The following transition labels are assumed. Their energy order is irrelevant.

$$\nu_1 = E_g^a \leftarrow B_{1g}; \quad \nu_2 = B_{2g} \leftarrow B_{1g}; \quad \nu_3 = A_{2g}^a \leftarrow B_{1g}; \quad \nu_4 = E_g^b \leftarrow B_{1g}$$

$$\nu_5 = A_{2g}^b \leftarrow B_{1g}; \quad \nu_6 = E_g^c \leftarrow B_{1g}$$

$$DS = -7Ds = \tfrac{1}{2}\{\nu_2 + 5(\nu_3 + \nu_5) - 4(\nu_1 + \nu_4 + \nu_6) - 15B\} \tag{A1}$$

$$DT = -\left(7\sqrt{15}\,Dt\right)/2 = \left(\sqrt{15}/20\right)\{11\nu_2 - (\nu_3 + \nu_5) - 2(\nu_1 + \nu_4 + \nu_6) + 45B\} \tag{A2}$$

$$DQ = \left(0.6\sqrt{21}\right)\nu_2 + \left(\sqrt{7}/\sqrt{5}\right)DT \tag{A3}$$

(N.B.; $10Dq = \nu_2$)

$$\begin{aligned} B = 1/990\big[&-(36\nu_1 - 54\nu_3 + 36\nu_4 - 54\nu_5 + 36\nu_6)\big] \\ &\pm\Big[(36\nu_1 - 54\nu_3 + 36\nu_4 - 54\nu_5 + 36\nu_6)^2 - 1980\big(\nu_2^2 + 3(\nu_3 + \nu_5)^2 \\ &+ 4(-\nu_1\nu_3 + \nu_1\nu_4 - \nu_1\nu_5 + \nu_1\nu_6 - \nu_3\nu_4 \\ &\qquad - \nu_3\nu_6 - \nu_4\nu_5 + \nu_4\nu_6 - \nu_5\nu_6)\big)\Big]^{1/2}. \end{aligned} \tag{A4}$$

(b) d^2 and d^7 $T_{1g}(F)$ ground term in O_h leading to two possible ground terms in D_{4h}.

(i) A_2 ground term in D_{4h}. The following transition labels are assumed.

$$\nu_1 = E_g^a \leftarrow A_{2g}^a; \quad \nu_2 = E_g^b \leftarrow A_{2g}^a; \quad \nu_3 = B_{2g} \leftarrow A_{2g}^a; \quad \nu_4 = B_{1g} \leftarrow A_{2g}^a$$

$$\nu_5 = A_{2g}^b \leftarrow A_{2g}^a; \quad \nu_6 = E_g^c \leftarrow A_{2g}^a$$

The relevant equations are

$$DS = -7Ds = -\tfrac{1}{2}\{(\nu_3 + \nu_4) + 5\nu_5 - 4(\nu_1 + \nu_2 + \nu_6) - 15B\} \tag{A5}$$

$$\begin{aligned} DT = -7\sqrt{15}\,Dt/2 = -\left(\sqrt{15}/20\right)\{&11\nu_3 - 3\nu_4 - \nu_5 \\ &-2(\nu_1 + \nu_2 + \nu_6) + 45B\} \end{aligned} \tag{A6}$$

$$DQ = \left(0.6\sqrt{21}\right)(\nu_4 - \nu_3) + \left(\sqrt{7}/\sqrt{5}\right)DT \tag{A7}$$

(N.B.; $10Dq = \nu_4 - \nu_3$)

(ii) E ground term in D_{4h}. The following transition labels are assumed.

$\nu_1 = A^{a}_{2g} \leftarrow E^{a}_{g}$; $\nu_2 = E^{b}_{g} \leftarrow E^{a}_{g}$; $\nu_3 = B_{2g} \leftarrow E^{a}_{g}$; $\nu_4 = B_{1g} \leftarrow E^{a}_{g}$
$\nu_5 = A^{b}_{2g} \leftarrow E^{a}_{g}$; $\nu_6 = E^{c}_{g} \leftarrow E^{a}_{g}$

The relevant equations are

$$DS = -7Ds = -\tfrac{1}{2}\{5(\nu_1+\nu_5) - 4(\nu_2+\nu_6) + (\nu_3+\nu_4) - 15B\} \tag{A8}$$

$$DT = -\left(7\sqrt{15}\,Dt\right)/2 = -\left(\sqrt{15}/20\right)\{11\nu_3 - 3\nu_4 - \nu_5 \\ -2(\nu_1+\nu_2+\nu_6) + 45B\} \tag{A9}$$

$$DQ = \left(0.6\sqrt{21}\right)(\nu_4 - \nu_3) + \left(\sqrt{7}/\sqrt{5}\right)DT \tag{A10}$$

(N.B.; $10Dq = \nu_4 - \nu_3$)

In these cases the energy order is again irrelevant. Note that the equations for DT and DQ are independent of ground term.

While expressions for evaluating B may be derived by appropriate substitution and expansion of eqn. (A4), this is most readily accomplished within the microcomputer programme. Thus for d^2, d^7, eqn. (A4) is programmed and the following substitution made within the programme: The superscript N identifies the transition energy in eqn. (A4)

A_2 ground term:

$\nu_1^N = \nu_1 - \nu_4$; $\nu_2^N = \nu_3 - \nu_4$; $\nu_3^N = -\nu_4$; $\nu_4^N = \nu_2 - \nu_4$
$\nu_5^N = \nu_5 - \nu_4$; $\nu_6^N = \nu_6 - \nu_4$

E ground term:

$\nu_1^N = -\nu_4$; $\nu_2^N = \nu_3 - \nu_4$; $\nu_3^N = \nu_1 - \nu_4$; $\nu_4^N = \nu_2 - \nu_4$
$\nu_5^N = \nu_5 - \nu_4$; $\nu_6^N = \nu_6 - \nu_4$

Two values of B will arise from solution of (A4). Generally the lower in magnitude (often negative) is incorrect. If there is any ambiguity it will be resolved upon calculation of the transition energies.

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43 Note that the entries for the elements $\langle E_g(\theta)|\hat{O}|E_g(\epsilon)\rangle$ and $\langle E_g(\theta)|\hat{O}|T_{2g}(xy)\rangle$ are incorrect in Table VIII of ref. 6. They should be replaced by $\langle x^2-y^2|O|z^2\rangle$ in Table 3 of this paper.