Electronic Supplementary Information for Dalton Transactions

Supplementary Data

Magnetic Circular Dichroism Spectroscopy of Antiferromagnetically Coupled Hetero-Metallic Rings $[H_2NR_2][Cr_7MF_8(O_2CCMe_3)_{16}]$

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Determination of the components of the lambda tensor

Calculation of the lambda tensor is greatly simplified by calculating the vector coupling coefficients in the octahedral group and treating the symmetry lowering distortions of the crystal field as a perturbation. The lambda tensor is made up of a sum of matrix elements describing the connection of the ground state to excited state terms via the orbital angular momentum operator. Each matrix element is decomposed into a reduced matrix element and a 3jm coefficient according to Wigner-Eckhart theorem.

$$\left\langle Sh\varphi \middle| \hat{L}_{\vartheta}^{T_{1g}} \middle| S'h'\phi' \right\rangle = \delta_{SS'} \begin{pmatrix} h \\ \vartheta \end{pmatrix} \begin{pmatrix} h\,T_1\,h' \\ \varphi\,\vartheta\,\varphi' \end{pmatrix} \left\langle {}^{2S+1}h \middle\| L^{T_{1g}} \middle\| {}^{2S'+1}h' \right\rangle \qquad \text{(S1)}$$

where S and S' are the ground and excited state spin angular momenta, h and h' the ground and excited state orbital angular momentum irreducible representations, h and h' the components of the ground and excited state irreducible representations, respectively, and θ is the component of the irreducible representation of the orbital angular momentum operator. The $\delta_{SS'}$ term accounts for the inability of the orbital angular momentum operators to mix states with different values of total spin.

All observed excited state terms of the d^3 configuration transform as E, T_1 or T_2 and in the octahedral point group the orbital angular momentum operator transforms as T_1. All 3jm coefficients coupling the A_2 ground state to E and T_1 excited states via the components of T_1 are zero. Therefore ${}^4T_2$ is the only low lying excited state which can contribute to the lambda tensor of a d^3 ion to second order of perturbation. $T_1(x)$ only connects A_2 with $T_2(\xi)$, $T_1(y)$ connects A_2 only with $T_2(\eta)$ and $T_1(z)$ connects A_2 only with $T_2(\zeta)$.

The non-zero matrix elements are then

$$
\begin{aligned}
\left\langle {}^4A_2 \left| L_x^{T1} \right| {}^4T_2\xi \right\rangle &= \left(\frac{A_2}{a_2} \right) \begin{pmatrix} A_2 & T_1 & T_2 \\ a_2 & x & \xi \end{pmatrix} \left\langle A_2 \left\| L^{T1} \right\| T_2 \right\rangle = 1 \cdot \frac{1}{\sqrt{3}} \cdot \left\langle A_2 \left\| L^{T1} \right\| T_2 \right\rangle \\
\left\langle {}^4A_2 \left| L_y^{T1} \right| {}^4T_2\eta \right\rangle &= \left(\frac{A_2}{a_2} \right) \begin{pmatrix} A_2 & T_1 & T_2 \\ a_2 & y & \eta \end{pmatrix} \left\langle A_2 \left\| L^{T1} \right\| T_2 \right\rangle = 1 \cdot \frac{1}{\sqrt{3}} \cdot \left\langle A_2 \left\| L^{T1} \right\| T_2 \right\rangle \\
\left\langle {}^4A_2 \left| L_z^{T1} \right| {}^4T_2\varsigma \right\rangle &= \left(\frac{A_2}{a_2} \right) \begin{pmatrix} A_2 & T_1 & T_2 \\ a_2 & z & \zeta \end{pmatrix} \left\langle A_2 \left\| L^{T1} \right\| T_2 \right\rangle = 1 \cdot \frac{1}{\sqrt{3}} \cdot \left\langle A_2 \left\| L^{T1} \right\| T_2 \right\rangle \\
\left\langle {}^4T_2\xi \left| L_x^{T1} \right| {}^4A_2 \right\rangle &= \left(\frac{T_2}{\xi} \right) \begin{pmatrix} T_2 & T_1 & A_2 \\ \xi & x & a_2 \end{pmatrix} \left\langle T_2 \left\| L^{T1} \right\| A_2 \right\rangle = -1 \cdot \frac{1}{\sqrt{3}} \cdot \left\langle T_2 \left\| L^{T1} \right\| A_2 \right\rangle \\
\left\langle {}^4T_2\eta \left| L_y^{T1} \right| {}^4A_2 \right\rangle &= \left(\frac{T_2}{\eta} \right) \begin{pmatrix} T_2 & T_1 & A_2 \\ \eta & y & a_2 \end{pmatrix} \left\langle T_2 \left\| L^{T1} \right\| A_2 \right\rangle = 1 \cdot \frac{1}{\sqrt{3}} \cdot \left\langle T_2 \left\| L^{T1} \right\| A_2 \right\rangle \\
\left\langle {}^4T_2\zeta \left| L_z^{T1} \right| {}^4A_2 \right\rangle &= \left(\frac{T_2}{\zeta} \right) \begin{pmatrix} T_2 & T_1 & A_2 \\ \zeta & z & a_2 \end{pmatrix} \left\langle T_2 \left\| L^{T1} \right\| A_2 \right\rangle = -1 \cdot \frac{1}{\sqrt{3}} \cdot \left\langle T_2 \left\| L^{T1} \right\| A_2 \right\rangle
\end{aligned}
\qquad \text{(S2)}
$$

The reduced matrix elements are then evaluated by equating the ${}^4A_2$ to ${}^4T_2$ transition to the difference between the two strong field configurations t_{2g}^3 and t_{2g}^2eg and applying the $SO_3 \supset O$ group chain. Since the spin independent unit tensor operator

$$\left\langle nl \left\| u^k \right\| n'l' \right\rangle \equiv \delta_{nn'}\delta_{ll'}$$

transforms as the $\left| jm \right\rangle$ of SO_3 the one electron reduced matrix elements for the angular momentum operator in SO_3 is simply related to this unit tensor.

$$\left\langle nl \left\| l \right\| n'l' \right\rangle = \delta_{nn'}\delta_{ll'} \cdot \left[l(l+1)(2l+1) \right]^{1/2} \qquad \text{(S3)}$$

Therefore,

$$
\begin{aligned}
\left\langle A_2 \left\| L^{T1} \right\| T_2 \right\rangle = \left\langle T_2 \left\| L^{T1} \right\| A_2 \right\rangle = \left\langle t_2 \left\| l^{t_1} \right\| e_g \right\rangle &= \begin{pmatrix} 2 & 1 & 2 \\ T_2 & T_1 & E \end{pmatrix}{}^{SO_3}_{O} \cdot \left[l(l+1)(2l+1) \right]^{1/2} \\
&= -\frac{\sqrt{2}}{\sqrt{5}} \cdot \sqrt{(2 \cdot 3 \cdot 5)} = -2\sqrt{3}
\end{aligned}
\qquad \text{(S4)}
$$

where the 3jm factor relates the matrix element of angular momentum in the SO_3 basis to that in O. Substitution of this value into equation A1 yields the components of the lambda tensor in octahedral symmetry. The corresponding components in the C_{2v} point group are calculated by applying the chain of groups approach to determine 3jm factors by which the above 3jm coefficients are multiplied in order to account for the lowering in symmetry. Following the chain

$O_h \supset D_{4h} \supset D_{2d} \supset C_{2v}$ yields the following branching of the electronic terms (the symbol in parenthesis being the label in the natural system corresponding to the given Mulliken label)

O_h	D_{4h}	D_{2d}	C_{2v}
$A_{2g}(\tilde{0})$ $B_{1g}(2)$	$B_2(2)$	$A_1(0)$	
$T_{1g}(1)$	$A_{2g}(\tilde{0})+E_g(1)$	$A_2(\tilde{0})+E(1)$	$A_2(\tilde{0})+B_1(1)+B_2(\tilde{1})$
$T_{2g}(\tilde{1})$	$B_{2g}(\tilde{2})+E_g(1)$	$B_1(\tilde{2})+E(1)$	$A_2(\tilde{0})+B_1(1)+B_2(\tilde{1})$

For example the 3jm coefficient

$\begin{pmatrix} A_2 & T_1 & T_2 \\ a_2 & x & \xi \end{pmatrix}$ becomes

$$\begin{pmatrix} A_{2g} & T_{1g} & T_{2g} \\ a_2 & x & \xi \end{pmatrix} \cdot \begin{pmatrix} A_{2g} & T_{1g} & T_{2g} \\ B_{1g} & E_g & E_g \end{pmatrix}\begin{matrix} O_h \\ D_{4h} \end{matrix} \cdot \begin{pmatrix} B_{1g} & E_g & E_g \\ B_2 & E & E \end{pmatrix}\begin{matrix} D_{4h} \\ D_{2d} \end{matrix} \cdot \begin{pmatrix} B_2 & E & E \\ A_1 & B_2 & B_2 \end{pmatrix}\begin{matrix} D_{2d} \\ C_{2v} \end{matrix}$$

$$= \begin{pmatrix} A_{2g} & T_{1g} & T_{2g} \\ a_2 & x & \xi \end{pmatrix} \cdot \sqrt{2}/\sqrt{3} \cdot 1 \cdot -1/\sqrt{2} = -1/\sqrt{3} \begin{pmatrix} A_{2g} & T_{1g} & T_{2g} \\ a_2 & x & \xi \end{pmatrix} \qquad \text{(S5)}$$

that is the 3jm coefficient of the octahedral group is multiplied by a factor of -1/√3 to account for the lowering of the symmetry to C_{2v}. Application of the above procedure to the remaining non-zero 3jm factors leads to the result,

$$\Lambda_{zz} = \frac{4}{3 \cdot \Delta E_1}; \Lambda_{yy} = \frac{4}{3 \cdot \Delta E_2}; \Lambda_{xx} = \frac{4}{3 \cdot \Delta E_3} \qquad \text{(S6)}$$

where $\Delta E_1 = E\left({}^4A_1 \rightarrow a\,{}^4A_2\right)$, $\Delta E_2 = E\left({}^4A_1 \rightarrow a\,{}^4B_1\right)$ and $\Delta E_3 = E\left({}^4A_1 \rightarrow a\,{}^4B_2\right)$