MCD of Uranyl D_{3h} and D_{5h} Complexes

C. GÖRLLER-WALRAND and W. COLEN

University of Leuven, Laboratory of Inorganic Chemistry, Celestijnenlaan 200F, 3030 Heverlee, Belgium

Received October 5, 1983

The aim of this note is to illustrate how the unique properties of circularly polarized light applied to the UO_2^{++} system in a magnetic field (MCD) can provide information on the identification of electronic states which are not readily deduced by other means. In EPR for example the sign and sense of the magnetic field is completely lost.

The spectra (see Fig. 1) for two types of equatorial non centro-symmetric complexation of the uranyl ion are discussed: the D_{5h} symmetry in $Cs_3UO_2F_5$ and the D_{3h} symmetry present in trinitrate complexes (example: $NBu_4UO_2(NO_3)_3$.

Only the induced electric dipole transitions are considered: they clearly dominate the spectrum by progressions in the symmetric stretching vibration of the UO_2^{++} ion (ν_s), as can be deduced from the comparison with centro-symmetric complexes *e.g.* $Cs_2UO_2Cl_4$.

Considerations on other intensity mechanisms can be found in papers previously published by Denning and co-workers [1–4] as well as by our group [5–7].

Comments on MCD and Sign of the A Term

One of the unusual features of the interaction of a magnetic field with molecules or ions is that transitions between the levels split by the field are allowed for circularly polarized light.

Indeed, electric dipole radiation has a well-defined total angular momentum J = 1 but only circularly polarized light has a well defined z component of angular momentum $M_J = -1$ and $M_J = +1$ for left and right circularly polarized light. These properties can be used to develop selection rules for absorption and emission based on the conservation of angular momentum. The classical example is that of a transition from ^1S atomic state (J = 0) to ^1P (J = 1).

In the absence of a magnetic field the transition takes place to give one absorption line for unpolarized radiation. The signal is related to the dipole strength (D) containing the transition moment or the matrix element in the transition operator, in our case, the electric dipole operator:

$$\epsilon = 108.9 D\nu f(\nu)$$

with D: dipole strength $= \dfrac{3}{2d_a} \sum_{j \leftarrow a} [|R_-|^2 + |R_+|^2]$

In a magnetic field the P state is split into its magnetic components. For circularly polarized light the selection rules indicate that there are two distinct transitions. Measurement of $\epsilon_l - \epsilon_r$ (the circular dichroism) yields the line shape shown in Fig. 2.

This band shape is called a Faraday A term and arises when the system possesses a degenerate ground or excited state.

The signal is now related to the A term that contains, besides a difference of transition moments, a difference of magnetic moments

$$\Delta\epsilon = -1.02\ 10^{-2} A\nu \frac{df(\nu)}{d\nu}$$

$$A = \frac{3}{2d_a} \sum_{j \leftarrow a} [\langle j^o|\mu_z|j^o\rangle(|R_-|^2 - |R_+|^2)]$$

In the example of $^1P \leftarrow {}^1S$ transition, left circularly polarized light will be absorbed between the $M_J = 0$ (^1S) component and $M_J = +1$ (^1P) component according to:

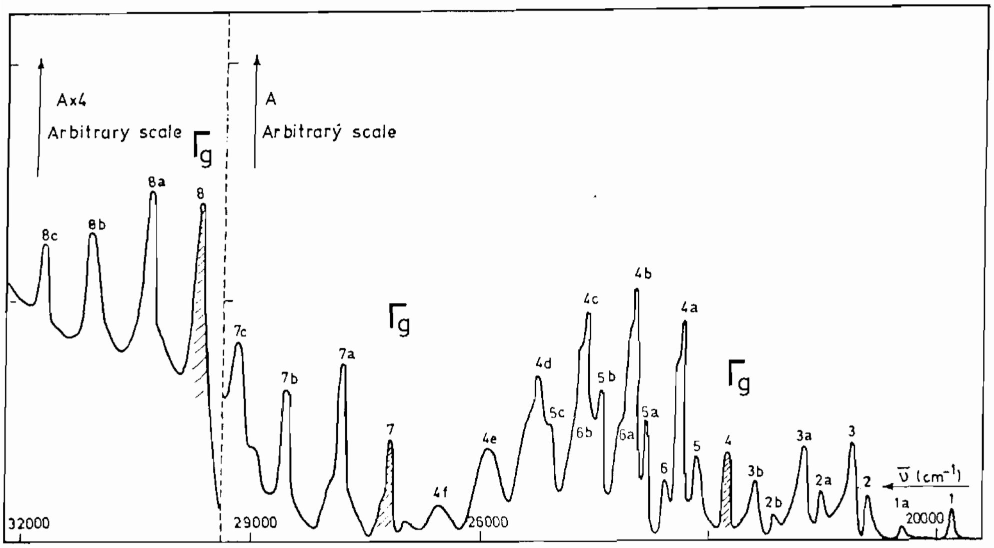
$$\langle \psi(JM_J)|R_\rho^{(1)}|\psi(J'M_J')\rangle =$$
$$= (-1)^{J-M_J} \begin{pmatrix} J & 1 & J' \\ -M_J & \rho & M_J' \end{pmatrix} \langle \psi(J)||R||\psi(J')\rangle$$

with $\rho = +1, -1$ for right and left circularly polarized light, while absorption of right circularly polarized light occurs between $M_J = 0$ and $M_J = -1$. At highest energy absorption between the components $M_J = 0$ (ground state) and $M_J = +1$ (excited state) occurs for left circularly polarized light, leading to a positive A term.

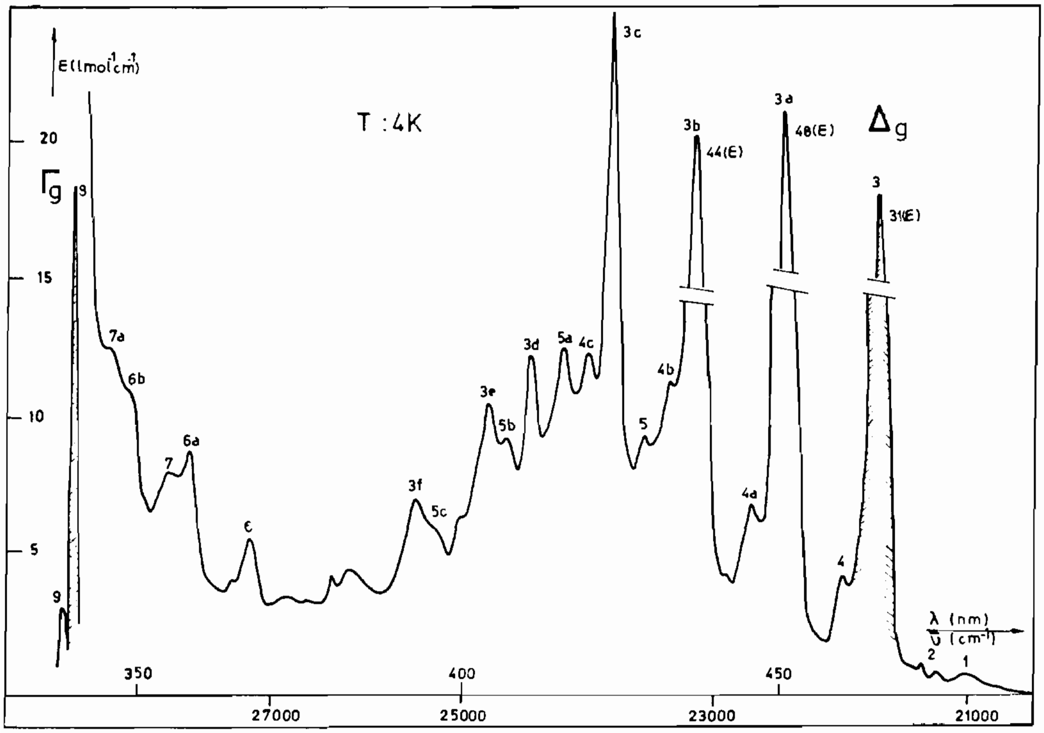
Application to the UO_2^{++} Ion in D_{3h} and D_{5h} Symmetry

In order to apply this to the UO_2^{++} complexes one has to keep in mind that before the Zeeman field is applied other perturbing fields are to be taken into

0020-1693/84/$3.00



(a)



(b)

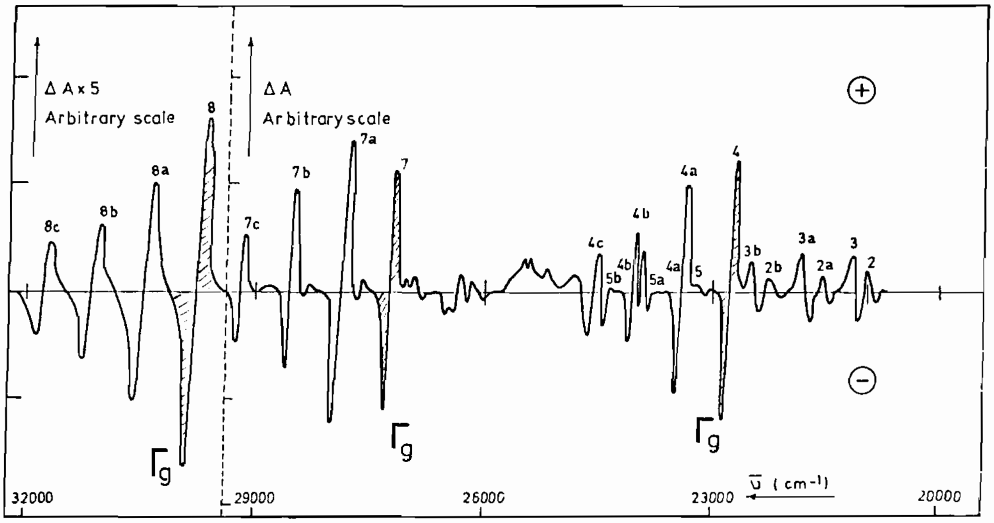
account: the electron repulsion (ER), spin orbit coupling (Soc) and crystal field (CF).

In the case of the UO_2^{++} the situation is complex, as the CF describes in fact on one side the axial field of the two oxygen atoms containing the linear entity, and on the other side the equatorial field of the other ligands whose coordinating atoms are usually situated in a plane perpendicular to the actinyl axis. The axial field V_{ax} is known to cause an extremely strong perturbation so that there is strong evidence that V_{ax} is larger than all other perturbations

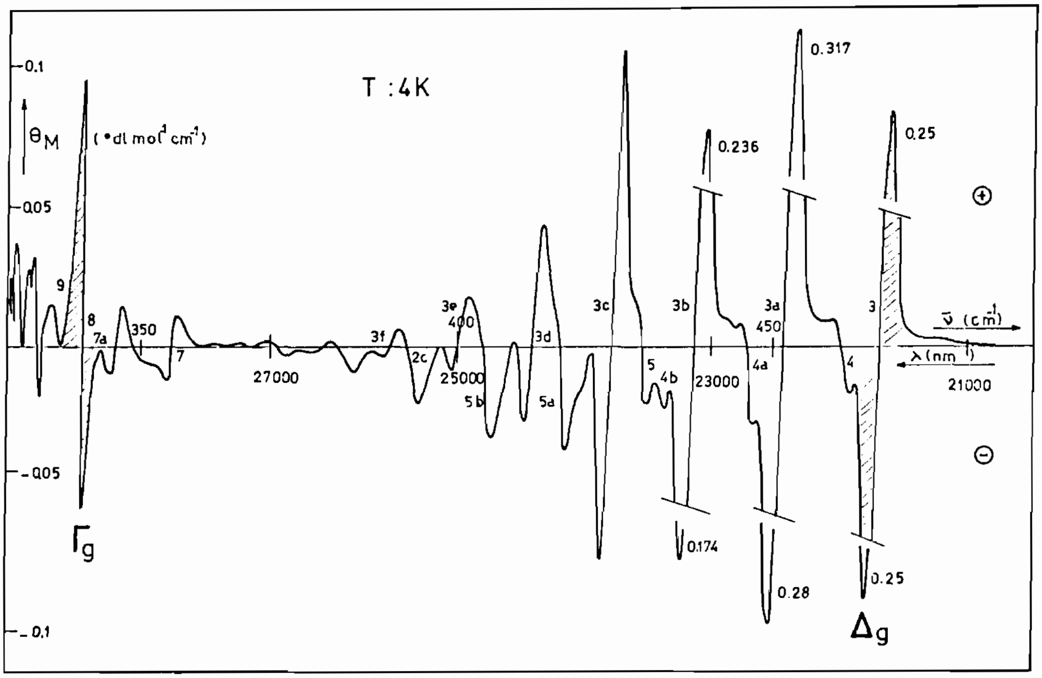
$$V_{ax} > ER > soc > V_{eq} > Zeeman$$

Consequently each molecular orbital will be characterized to a good approximation in $D_{\infty h}$ by the quantum number λ.

Almost any theoretical treatment of the uranyl ion agrees in predicting that the two upper occupied

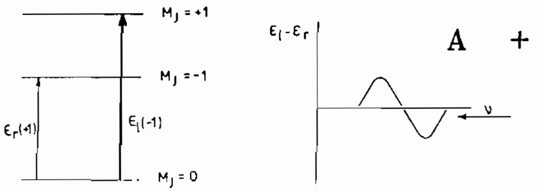


(c)



(d)

Fig. 1. Absorption and MCD spectra of $Cs_3UO_2F_5$ and $NBu_4UO_2(NO_3)_3$. (a) Absorption spectrum of $Cs_3UO_2F_5$ in silicon grease. (b) Absorption spectrum of $NBu_4UO_2(NO_3)_3$ in PMMA. (c) MCD spectrum of $Cs_3UO_2F_5$ in silicon grease. (d) MCD spectrum of $NBu_4UO_2(NO_3)_3$ in PMMA.



At highest frequency the transition is allowed for left circularly polarized light between M =0 (ground state) and M =+1 (excited state)

Fig. 2. Line shape yielding from measurement of $\epsilon_l - \epsilon_r$— the positive A term.

orbitals in the ground state are π_u and σ_u^+ while the two lowest unoccupied are the non bonding f orbitals ϕ_u and δ_u.

The ground state is thus:

$$\ldots (\pi_u)^4(\sigma_u^+)^2 \quad {}^1\Sigma_g^+$$

while a series of states arise from the excited configuration. Within a $\Lambda - \Sigma$ Russell–Saunders coupling scheme the states are given in Table I, with the magnetic moments and correlations of the irreducible representations in the $D_{\infty h}$, D_{3h} and D_{5h} groups. If the transition between the totally symmetric ground state and the excited state is allowed electronically, its polarization in D_{3h} and D_{5h} is given in parentheses. Obviously, no pure electric dipole transitions can be found as all transitions are parity-forbidden. Electric dipole transitions are allowed to the extent that states of opposite parity are mixed in the f-states. Following the Judd and Ofelt theory, the simplest mechanism for inducing intensity is the coupling of states of opposite parity by way of the odd terms in the crystal field.

For a pure electric dipole transition in the UO_2^{++} spectrum (for example a hypothetical ${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$ transition) the matrix element in the electric dipole operator will be given by

TABLE I. Electronic States, Magnetic Moments (in $D_{\infty h}$) and Correlation Representations in D_{3h} and D_{5h}. (If the Transition Between the Totally Symmetric Ground State and the Excited State is Electronically Allowed, its Polarization is given in Parenthesis).

Electron configuration	Symmetry in $D_{\infty h}$		Magnetic moment (β)	Symmetry in D_{3h}	Symmetry in D_{5h}
$\sigma\delta$	${}^1\Delta$	Δ	-2	$E'(x, y)$	E_2'
$\sigma\delta$	${}^3\Delta$	Φ	-4	A_1'', $A_2''(z)$	E_2''
		Δ	-2	$E'(x, y)$	E_2'
		Π	0	E''	E_1''
$\sigma\phi$	${}^1\Phi$	Φ	-3	A_1'', $A_2''(z)$	E_2''
$\sigma\phi$	${}^3\Phi$	Γ	-5	$E'(x, y)$	$E_1'(x, y)$
		Φ	-3	A_1'', $A_2''(z)$	E_2''
		Δ	-1	$E'(x, y)$	E_2'
$\pi^3\delta$	${}^1\Phi$	Φ	-3	A_1'', $A_2''(z)$	E_2''
$\pi^3\delta$	${}^3\Phi$	Γ	-5	$E'(x, y)$	$E_1'(x, y)$
		Φ	-3	A_1'', $A_2''(z)$	E_2''
		Δ	-1	$E'(x, y)$	E_2'
$\pi^3\delta$	${}^1\Pi$	Π	-1	E''	E_1''
$\pi^3\delta$	${}^3\Pi$	Δ	-3	$E'(x, y)$	E_2'
		Π	-1	E''	E_1''
		Σ^+, Σ^-	$[+1]$	A_1'	A_1'
$\pi^3\phi$	${}^1\Gamma$	Γ	-4	$E'(x, y)$	$E_1'(x, y)$
$\pi^3\phi$	${}^3\Gamma$	H	-6	E''	A_1'', $A_2''(z)$
		Γ	-4	$E'(x, y)$	$E_1'(x, y)$
		Φ	-2	A_1'', $A_2''(z)$	E_2''
$\pi^3\phi$	Δ	Δ	-2	$E'(x, y)$	E_2'
$\pi^3\phi$	${}^3\Delta$	Φ	-4	A_1'', A_2''	E_2''
		Δ	-2	$E'(x, y)$	E_2'
		Π	0	E''	E_1''

$$\langle\psi(\Omega M_\Omega)|R_\rho^{(1)}|\psi(\Omega' M_\Omega')\rangle = = (-1)^{\Omega - M_\Omega}\begin{pmatrix}\Omega & 1 & \Omega' \\ -M_\Omega & \rho & M_\Omega'\end{pmatrix}\langle\psi(\Omega)||R^{(1)}||\psi(\Omega')\rangle$$

with: $\Omega = (\Lambda + \Sigma)$: total angular momentum quantum number in $D_{\infty h}$ symmetry; M_Ω: component along the z axial field axis.

For a forced electric dipole transition the matrix element will be proportional, besides a series of factors not explained here [8], to a 3j-symbol including the symmetry dependent component q:

$$\langle\psi(\Omega M_\Omega)|R_\rho^{(1)}|\psi(\Omega' M_\Omega')\rangle = \ldots\langle\psi(\Omega M_\Omega)|U^\lambda_{\rho+q}|\psi(\Omega M_\Omega')\rangle = \ldots(-1)^{\Omega - M_\Omega}\begin{pmatrix}\Omega & \lambda & \Omega' \\ -M_\Omega & \rho+q & M_\Omega'\end{pmatrix}\langle\psi(\Omega)||U^\lambda||\psi(\Omega')\rangle$$

with: k, q: rank and component of the odd terms in the expansion of the crystal field potential:

$$V = \sum_{kqi} B_q^{(k)}(C_q^{(k)})_i$$

with: $\lambda = 2$ for $k = 1, 3$; $\lambda = 4$ for $k = 3, 5$; $\lambda = 6$ for $k = 5, 7$.

The crystal field potential for the D_{3h} and D_{5h} symmetry includes the following terms:

$V_{D_{5h}}$: even: $B_o^o B_o^2 B_o^4 B_o^6$

odd: B_5^5

D_{3h}: even: $B_o^o B_o^2 B_o^4 B_o^6 B_6^6$

odd: $B_3^3 B_3^5$

The even term B_6^6 is responsible for the mixing in D_{3h}:

$$(\Delta_{g_{\pm 2}}|C_{\pm 6}^6|\Gamma_{g_{\mp 4}})$$

The odd terms in both D_{3h} and D_{5h} induce intensity because of the mixing:

in D_{5h}: $\langle\Gamma_{g_{\pm 4}}|C_{\pm 5}^5|\Pi_{u_{\mp 1}}\rangle \ldots$

$$\text{in } D_{3h}: \begin{cases}\langle\Delta_{g_{\pm 2}}|C_{\pm 3}^{3,5}|\Pi_{u_{\mp 1}}\rangle \\ \langle\Gamma_{g_{\mp 4}}|C_{\mp 3}^{3,5}|\Pi_{u_{\mp 1}}\rangle\end{cases}$$

The transition moments are related to the following 3-j symbols:

$$\langle\psi(\Omega M_\Omega|R_\rho^{(1)}|\psi(\Omega' M_{\Omega'})\rangle = \ldots\begin{pmatrix}\Omega & \lambda & \Omega' \\ -M_\Omega & \rho+q & M_\Omega'\end{pmatrix}$$

$$\text{For } D_{5h} \quad \Gamma_g \longleftarrow {}^1\Sigma_g\begin{pmatrix}0 & 4 \text{ or } 6 & 4 \\ 0 & \mp 1 \pm 5 & \mp 4\end{pmatrix} \quad A-$$

$$\text{For } D_{3h} \begin{cases}\Gamma_g \longleftarrow {}^1\Sigma_g\begin{pmatrix}0 & 4 \text{ or } 6 & 4 \\ 0 & \pm 1 \pm 3 & \mp 4\end{pmatrix} \quad A+ \\ \Delta_g \longleftarrow {}^1\Sigma_g\begin{pmatrix}0 & 2 \text{ or } 4 & 2 \\ 0 & \mp 1 \pm 3 & \mp 2\end{pmatrix} \quad A-\end{cases}$$

This means that for $\Gamma_g \leftarrow {}^1\Sigma_g^+$ in D_{5h} absorption at the highest frequency occurs between the components $M_\Omega = 0$ (ground state) and $M_\Omega = +4$ (excited state) for right circularly polarized light leading to a negative A term, while in D_{3h} absorption at the highest frequency occurs between $M_\Omega = 0$ and $M_\Omega = +4$ for left circularly polarized light leading to a positive A term (Fig. 3).

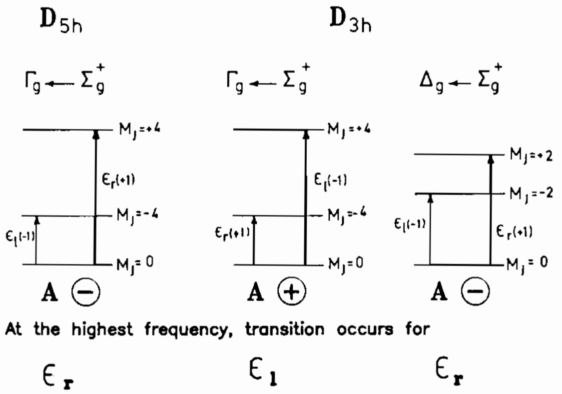


Fig. 3. Sign of the A terms for the induced electric dipole transitions.

In a similar way for $\Delta_g \leftarrow {}^1\Sigma_g^+$ in D_{3h} negative A terms are found, because at the highest energy the transition between $M_\Omega = 0$ and $M_\Omega = +2$ occurs for right circularly polarized light.

By looking at the peaks that dominate the spectrum of $Cs_3UO_2F_5$ one finds three progressions in the symmetric stretching vibration (ν_s) that clearly exhibit negative A terms and correspond in our hypothesis to Γ_g states (see Fig. 1).

On the other side in the spectrum of $UO_2(NO_3)_3^-$ a progression appears with negative A terms that should be a Δ_g state while in the region at 29585 cm^{-1} a progression is found with positive A terms. This should be the homolog of the negative A signal at 29755 cm^{-1} in $Cs_3UO_2F_5$ (see Fig. 1).

We emphasize that the sign argumentation developed here to identify the Δ_g and Γ_g states in D_{3h} and D_{5h} complexes is supported by other considerations, including data on the vibronic coupling and polarization as well as calculation of magnetic moments [7].

Acknowledgements

This work is supported through grants from the IWONL and FKFO Belgium. The authors are indebted to the Belgian Government (Programmatie van het Wetenschapsbeleid). We thank F. Morissens for his technical help, and Prof. Nguyen Quy Dao for the $Cs_3UO_2F_5$ crystals.

References

1 R. G. Denning, T. R. Snellgrove and D. R. Woodwark, *Mol. Phys. 30*, 1819 (1975).
2 R. G. Denning, T. R. Snellgrove and D. R. Woodward, *Mol. Phys., 32*, 419 (1976).
3 R. G. Denning, D. N. P. Foster, T. R. Snellgrove and D. R. Woodwark, *Mol. Phys., 37*, 1089 (1979).
4 R. G. Denning, T. R. Snellgrove and D. R. Woodwark, *Mol. Phys., 37*, 1109 (1979).
5 C. Görller-Walrand and L. G. Vanquickenborne, *J. Chem. Phys., 54*, 4178 (1971).
6 C. Görller-Walrand and L. G. Vanquickenborne, *J. Chem. Phys., 57*, 1436 (1972).
7 C. Görller-Walrand, W. Colen and Nguyen Quy Dao, *J. Chem. Phys., 76*, 13 (1982).
8 R. D. Peacock, *Structure and Bonding, 22*, 83 (1975).