state may occur in the analogous $Pt(mnt)_2^{3-}$ species.

Registry No. $Ni(mnt)_2^{3-}$, 38117-63-4; $Pd(mnt)_2^{2-}$, 19555-33-0; $Pd(mnt)_2^{3-}$, 62906-14-3; $Pt(mnt)_2^{2-}$, 15152-99-5; $Pt(mnt)_2^{3-}$, 62906-13-2; $Pt(mnt)_2^{4-}$, 62906-12-1.

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An Angular Overlap Treatment of σ and π Bonding in f-Orbital Compounds

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By use of the recently published f-orbital angular transformation matrix, the angular overlap treatment is extended to embrace both σ and π (and higher λ) interactions in f-orbital compounds. Results are listed for a number of geometries, especially those commonly encountered in 4f and 5f complexes, and applied in particular to the estimation of the relative contributions of σ and π interactions in octahedral hexahalo species.

Introduction

The angular overlap model, first propounded by Jorgensen, Pappalardo, and Schmidtke,[1] was originally introduced in an attempt to understand the small 4f ligand field splittings observed for various complexes of the lanthanide series. Thus, it was argued, considering only σ-bonding effects, that such splittings were better interpreted in terms of a number of one-electron f-orbital energies (depending upon a single parameter characteristic of the ligands), rather than by use of a symmetry-determined number of $A_k^q\langle r^k\rangle$ parameters, arising from the electrostatic treatment. Subsequently, by use of the equivalent singular-contact potential method, this approach was extended to include also the effects of π-bonding interactions,[2] but the necessary general angular transformation matrices required were given only for the cases $l = 1$ and $l = 2$, the results listed being restricted to p- and d-orbital systems. Thereafter, although reference has been made[3] to the existence of the required f-orbital transform, the results for the case $l = 3$ have only recently become generally available, as given by Clack and Smith.[4]

Consequently it is now possible to consider via the angular overlap model the effects of π bonding (and in principle the higher λ interactions of δ and ϕ symmetry) for f-orbital systems as well to treat σ interactions not previously investigated, and the results are now given for a variety of geometric arrangements known to occur in the 4f and 5f series. These

include systems containing two–nine ligands, and examples belong to the point groups $D_{\infty h}$, D_{3h}, D_{4h}, D_{5h}, D_{6h}, T_d, and O_h. In general the results are confined to ML_N systems with all N ligands equivalent, but possible extensions to nonequivalent situations are noted in some instances.

Theory

The theory of the angular overlap model[1-3] has recently been succinctly summarized by Gerloch and Slade,[5] and only a brief outline of its conclusions is now therefore given. Thus one considers a chromophore, ML_N, where N is the number of coordinated ligands (L), l is the azimuthal quantum number for the orbitals of the metal (M) under consideration, and λ denotes the component of the angular momentum of any given molecular orbital about the internuclear axis (for $\lambda = 0$, 1, 2, 3, ... one has respectively σ, π, δ, ϕ, ... interactions). Assuming that the ligand orbitals lie energetically below those of the metal and that all the ligands are equivalent with no ligand λ orbital interacting with two nondegenerate metal orbitals, the antibonding energies of the metal l orbitals may be written as

$$E^* = e_\lambda \sum_{j=1}^{N} (F_\lambda{}^l)^2$$

where the e_λ quantities depend only on the radial functions of the metal and of the ligands and on the bond distance and

Table I. ML_N Systems Diagonal in E^*: Energies of f Orbitals in Units of e_λ

f orbital	Irreducible representation	e_σ	e_π	e_δ	e_ϕ
	ML_2, Axial, $D_{\infty h}$				
z^3	σ_u^+	2	0	0	0
xz^2	π_u {	0	2	0	0
yz^2		0	2	0	0
$z(x^2-y^2)$	δ_u {	0	0	2	0
xyz		0	0	2	0
$x(x^2-3y^2)$	ϕ_u {	0	0	0	2
$y(3x^2-y^2)$		0	0	0	2
	ML_3, Trigonal, D_{3h}				
z^3	a_2''	0	$9/8$	0	$15/8$
xz^2	e' {	$9/16$	$3/32$	$15/16$	$45/32$
yz^2		$9/16$	$3/32$	$15/16$	$45/32$
$z(x^2-y^2)$	e'' {	0	$15/16$	$3/2$	$9/16$
xyz		0	$15/16$	$3/2$	$9/16$
$x(x^2-3y^2)$	a_1'	$15/8$	0	$9/8$	0
$y(3x^2-y^2)$	a_2'	0	$45/16$	0	$3/16$
	ML_5, Pentagonal, D_{5h}				
z^3	a_2''	0	$15/8$	0	$25/8$
xz^2	e_1' {	$15/16$	$5/32$	$25/16$	$75/32$
yz^2		$15/16$	$5/32$	$25/16$	$75/32$
$z(x^2-y^2)$	e_2'' {	0	$25/16$	$5/2$	$15/16$
xyz		0	$25/16$	$5/2$	$15/16$
$x(x^2-3y^2)$	e_2' {	$25/16$	$75/32$	$15/16$	$5/32$
$y(3x^2-y^2)$		$25/16$	$75/32$	$15/16$	$5/32$

are independent of angular quantities. In general however E^* may contain off-diagonal terms, and its matrix elements are written[2,5] as

$$\langle \Psi_M \| \Psi_{M'} \rangle = \sum_\lambda \sum_\omega \sum_{j=1}^{N} e_{\lambda\omega j} F_{\lambda\omega}{}^l(\Psi_M) e_{\lambda\omega j} F_{\lambda\omega}{}^l(\Psi_{M'})$$

where, for $l = 3$, the required $F_{\lambda\omega}{}^l$ quantities are the elements of the general angular transformation matrix given by Clack and Smith.[4] The f-orbital set is here taken as the real orbitals f_{z^3} ($m_l = 0$), f_{xz^2}, f_{yz^2} (± 1), $f_{z(x^2-y^2)}$, f_{xyz} (± 2), and $f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$ (± 3), as defined by Friedman, Choppin, and Feuerbacher;[6] the summation in λ runs over the σ, π, δ, and ϕ ($m_l = 0$, ± 1, ± 2, and ± 3) contributions and that in ω over both components of the not necessarily degenerate $\pm m_l$ pair, while the index j runs over all the N ligands, whose positions are defined by the polar angles, θ_j and ϕ_j. The respective e_λ quantities are constant when the N ligands are identical and equidistant from M, while for any given f orbital, Ψ_M, the $F_{\lambda\omega}$ are the coefficients of the orbitals, characterized by λ ($=\sigma$, π, δ, or ϕ) and by ω ($=\cos$ or $\sin$), into which it is carried by the general angular transformation.

Frequently the matrices of E^* are entirely diagonal, and the ligand contributions therefore additive, as demonstrated by Schaffer and Jorgensen.[2] Thus the energies of the metal orbitals in an ML_N complex may be obtained by summing the energies in $ML_{N'}$ and $ML_{N''}$, where $N = N' + N''$. In some cases however the E^* matrices contain off-diagonal elements, so that the eigenvalues must be obtained by diagonalization; nevertheless, in such situations the additivity principle may be applied by the addition of the complete $ML_{N'}$ and $ML_{N''}$ matrices prior to diagonalization. In all geometries however the eigenvalues may readily be checked since the coefficients of the e_λ values must fulfill simple sum rules;[2] thus, for a given Ψ_M

$$\sum_\lambda e_\lambda = N$$

and for a given λ

$$\sum_{M=1}^{2l+1} e_\lambda = N \; (\lambda = 0) \text{ or } 2N \; (\lambda > 0)$$

Table II. ML_N Systems Nondiagonal in E^*: Matrices and Energies of f Orbitals in Units of e_λ

Matrices

	Diagonal matrix elements					Off-diagonal matrix elements
z^3	xz^2 $=yz^2$	$z(x^2-y^2)$	xyz	$x(x^2-3y^2)$ $=y(3x^2-y^2)$		$\langle xz\|x(x^2-3y^2)\rangle$ $=-\langle yz\|y(3x^2-y^2)\rangle$
			ML_4, D_{4h}			
e_σ 0	$3/4$	0	0	$5/4$		$-1/4(15^{1/2})$
e_π $3/2$	$1/8$	$5/2$	0	$15/8$		$1/8(15^{1/2})$
e_δ 0	$5/4$	0	4	$3/4$		$1/4(15^{1/2})$
e_ϕ $5/2$	$15/8$	$3/2$	0	$1/8$		$-1/8(15^{1/2})$
			ML_4, T_d			
e_σ $16/27$	$2/9$	0	$20/9$	$10/27$		$-2/27(15^{1/2})$
e_π $4/9$	$14/9$	$20/9$	0	$10/9$		$2/9(15^{1/2})$
e_δ $20/9$	$10/9$	$4/9$	0	$14/9$		$-2/9(15^{1/2})$
e_ϕ $20/27$	$10/9$	$4/3$	$16/9$	$26/27$		$2/27(15^{1/2})$
			ML_6, O_h			
e_σ 2	$3/4$	0	0	$5/4$		$-1/4(15^{1/2})$
e_π $3/2$	$17/8$	$5/2$	0	$15/8$		$1/8(15^{1/2})$
e_δ 0	$5/4$	2	6	$3/4$		$1/4(15^{1/2})$
e_ϕ $5/2$	$15/8$	$3/2$	0	$17/8$		$-1/8(15^{1/2})$

Eigenvalues

f orbital	Irreducible representation	ML_4, tetragonal, D_{4h}			
		e_σ	e_π	e_δ	e_ϕ
z^3	a_{2u}	0	$3/2$	0	$5/2$
xz^2	b_{1u}	0	0	4	0
yz^2	b_{2u}	0	$5/2$	0	$3/2$
$z(x^2-y^2)$	e_{2u} {	0	0	2	2
xyz		0	0	2	2
$x(x^2-3y^2)$	e_{2u} {	2	2	0	0
$y(3x^2-y^2)$		2	2	0	0

Cubic f orbital	Irreducible representation	ML_4, tetrahedral, T_d			
		e_σ	e_π	e_δ	e_ϕ
z^3	t_2 {	$16/27$	$4/9$	$20/9$	$20/27$
x^3		$16/27$	$4/9$	$20/9$	$20/27$
y^3		$16/27$	$4/9$	$20/9$	$20/27$
$z(x^2-y^2)$	t_1 {	0	$20/9$	$4/9$	$4/3$
$y(z^2-x^2)$		0	$20/9$	$4/9$	$4/3$
$x(z^2-y^2)$		0	$20/9$	$4/9$	$4/3$
xyz	a_1	$20/9$	0	0	$16/9$

Cubic f orbital	Irreducible representation	ML_6, octahedral, O_h			
		e_σ	e_π	e_δ	e_ϕ
z^3	t_{1u} {	2	$3/2$	0	$5/2$
x^3		2	$3/2$	0	$5/2$
y^3		2	$3/2$	0	$5/2$
$z(x^2-y^2)$	t_{2u} {	0	$5/2$	2	$3/2$
$y(z^2-x^2)$		0	$5/2$	2	$3/2$
$x(z^2-y^2)$		0	$5/2$	2	$3/2$
xyz	a_{2u}	0	0	6	0

Results

In Tables I and II are listed the results for the geometries ML_2, axial, $D_{\infty h}$; ML_3, trigonal, D_{3h}; ML_4, tetragonal, D_{4h}; ML_4, tetrahedral, T_d; ML_5, pentagonal, D_{5h}; and ML_6, octahedral, O_h. The results for the ML_6, hexagonal, D_{6h}, and the ML_8, cubic, O_h, situations are easily found to be exactly twice those of the ML_3, trigonal, and the ML_4, tetrahedral, cases, respectively. For the ML_2, ML_3, and ML_5 systems the E^* matrices are entirely diagonal, but in the remaining geometries off-diagonal elements are found, and the appropriate table lists all the nonvanishing matrix elements, as well as the resulting eigenvalues.

For systems giving diagonal E^* matrices the additivity principle is readily applied; thus the results for an ML_7 compound of D_{5h}, pentagonal bipyramidal, symmetry are derived immediately by summing the ML_2 and ML_5 contributions. On the other hand to obtain the octahedral ML_6

Table III. Energies of f Orbitals in Units of e_λ for ML$_9$ Systems of D_{3h} Symmetry[a]

f orbital	Irreducible representation	e_σ	e_π	e_δ	e_ϕ
z^3	a_2''	$3/16$	$117/32$	$45/16$	$75/32$
xz^2	e' {	$117/64$	$213/128$	$195/64$	$315/128$
yz^2		$117/64$	$213/128$	$195/64$	$315/128$
$z(x^2-y^2)$	e'' {	$45/32$	$195/64$	$51/32$	$189/64$
xyz		$45/32$	$195/64$	$51/32$	$189/64$
$x(x^2-3y^2)$	a_1'	$75/32$	$45/64$	$117/32$	$147/64$
$y(3x^2-y^2)$	a_2'	0	$135/32$	$9/4$	$81/32$

[a] In terms of the parameters of ref 1 this system is defined by $\chi = \xi = 2^{-1/2}$ and $\alpha = 45°$.

Figure 1. Splitting pattern for f orbitals of ML$_4$ systems in T_d symmetry. $E_1 = 4(11e_\sigma - 3\ e_\pi)/27, E_2 = 16(e_\sigma - 3e_\pi)/27$.

result from the ML$_2$ and the tetragonal ML$_4$ values it is necessary to add the complete matrices. When the axial and equatorial ligands are identical and equidistant from the metal, the eigenvalues are obviously those of the ML$_6$, O_h, situation, but when the axial and equatorial ligands differ, as for example in *trans*-MX$_2$Y$_4$ systems, e_λ parameters must be ascribed to both X and Y ligands and the eigenvalues obtained by numerical diagonalization.

In Tables I and II the symmetry designations of the seven f orbitals are given in each case, and the coefficients of the e_λ quantities indicate the extent to which these irreducible representations may participate in σ, π, δ, and ϕ bonding, respectively. Since the vast majority of ligands utilize only s and p orbitals in bonding to the metal, consideration is given only to the σ and π contributions; for each irreducible representation the allowed or forbidden character of the σ and π interaction with the f orbitals, as indicated by the e_λ coefficients, is in agreement with the results tabulated by Eisenstein,[7] in cases there treated, except that for the ML$_4$, D_{4h}, situation in which the π ligand orbitals should contain the representation b$_{2u}$ instead of b$_{1u}$.

For systems belonging to the cubic point groups, O_h and T_d, the f-orbital set contains threefold degenerate representations, the former transforming as a$_{2u}$ + t$_{1u}$ + t$_{2u}$, and the latter as a$_1$ + t$_1$ + t$_2$. However, in these geometries the real f orbitals, based on the $\pm m_l$ combinations,[6] are not all satisfactory basis functions, and there may instead be defined the cubic set δ (f$_{z^3}$, f$_{x^3}$, f$_{y^3}$), β (f$_{xyz}$), and ϵ (f$_{z(x^2-y^2)}$, f$_{y(z^2-x^2)}$, f$_{x(z^2-y^2)}$), where

$$f_{x^3} = -1/4\ \{6^{1/2}f_{xz^2} - 10^{1/2}f_{x(x^2-3y^2)}\}$$

$$f_{y^3} = -1/4\ \{6^{1/2}f_{yz^2} + 10^{1/2}f_{y(3x^2-y^2)}\}$$

$$f_{x(z^2-y^2)} = 1/4\ \{10^{1/2}f_{xz^2} + 6^{1/2}f_{x(x^2-y^2)}\}$$

$$f_{y(z^2-x^2)} = 1/4\ \{10^{1/2}f_{yz^2} - 6^{1/2}f_{y(3x^2-y^2)}\}$$

A further check is thereby provided for the T_d and O_h results since the eigenvectors resulting from diagonalization of the E^* matrices yield, as expected, the cubic functions listed above. For the ML$_4$, D_{4h}, system the f-orbital set contains two e$_{2u}$ irreducible representations; thus, by use of the real ($\pm m_l$) basis set the eigenfunctions obtained by diagonalization of the E^* matrices correspond to mixtures of the $m_l = \pm 2$ and ± 3 orbitals.

Discussion

There have recently appeared a number of detailed reviews[8–12] dealing with the coordination chemistry and geometry of lanthanide and actinide compounds, from which it is clear that in the former series the lower coordination numbers and simpler geometries are but rarely encountered. Thus in the 4f series by far the most common arrangement is that exemplified by the LnCl$_3$ systems, in which the metal is nine-coordinate; here six ligands constitute a trigonal prism
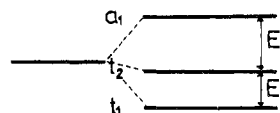
while three lie in an equilateral triangle parallel to the other two triangles though rotated by 60°, the overall symmetry being D_{3h}. For such systems the results of the angular overlap treatment, including π bonding, are given in Table III, but it is disappointing to note that the inclusion of π contributions does not produce any significant improvement on the correlations obtained earlier,[1] in which only σ bonding was considered. Possibly the difficulty in determining accurately the four B_q^k parameters required is at least partly responsible.

However, there are a fair number of ML$_6$, octahedral, species known for the 4f series, including especially the Cs$_2$NaLnCl$_6$ salts and the [Er(NCS)$_6$]$^{3-}$ anion, and it is also probable that the [TbF$_7$]$^{3-}$ anion is of pentagonal-bipyramidal, D_{5h}, symmetry. Similarly in the 5f series there exists a wide range of octahedral, ML$_6$, complexes, and the pentagonal-bipyramidal arrangement is also found in [UF$_7$]$^{3-}$ and in [UO$_2$F$_5$]$^{3-}$. It is in addition possible that some tetrahalides, such as UCl$_4$ and UBr$_4$, may be tetrahedral in the gas phase or in frozen-gas matrices, and systems such as [PaF$_8$]$^{3-}$ and [UF$_8$]$^{3-}$ are known to approximate closely to the cubic, O_h, ML$_8$ arrangement.

Since the angular overlap results for cubic ML$_8$ systems are simply double the corresponding values for the tetrahedral ML$_4$ complexes, it is only necessary to consider in detail the splitting patterns for the ML$_4$, tetrahedral, ML$_7$, pentagonal-bipyramidal, and ML$_6$, octahedral, geometries. For mixed-ligand systems, such as the D_{4h} [UCl$_4$Br$_2$]$^{2-}$, the model may be applied, via the additivity principle, as long as some estimate of the relative magnitudes of the e_λ parameters for Cl and Br ligands may be obtained (vide infra).

ML$_4$ Systems, Tetrahedral, T_d. When only σ bonding is considered, the antibonding energies of the f orbitals follow the sequence t$_1$ ($z(x^2-y^2)$ etc.) < t$_2$ (z^3 etc.) < a$_1$ (xyz) (cf. ref 1), but when π contributions are taken into account, the splittings are as shown in Figure 1, in which either the t$_1$ or the t$_2$ level may lie lowest, depending upon whether e_σ is greater or less than $3e_\pi$, the $E(t_2) - E(t_1)$ energy gap being $(e_\sigma - 3e_\pi)16/27$. Frequently e_π is found[3] to be of the order of $0.25e_\sigma$, but the octahedral 5f hexahalo complexes (quod vide) yield e_π/e_σ ratios of 0.4 or larger, so that no unequivocal answer may be given to this question. On the other hand the $E(a_1) - E(t_2)$ separation amounts to $(11e_\sigma - 3e_\pi)4/27$, and the $E(a_1) - E(t_1)$ gap to $(e_\sigma - e_\pi)20/9$, so that the a$_1$ level will clearly always lie highest. Finally it should be noted that when applying the T_d results (×2) to the cubic ML$_8$ situation the symmetry labels should be transposed in the sense a$_1 \rightarrow$ a$_{2u}$, t$_1 \rightarrow$ t$_{2u}$, and t$_2 \rightarrow$ t$_{1u}$.

ML$_7$ Systems, Pentagonal Bipyramidal, D_{5h}. Considering only σ bonding the energy ordering is here predicted to be e$_2''$ < e$_1'$ < e$_2'$ < a$_2''$, but in this case it is most improbable that the sequence could be disturbed by the inclusion of π bonding; thus the $E(a_2'') - E(e_2')$ separation amounts to $(14e_\sigma - 15e_\pi)/32$, which would require $e_\pi \sim e_\sigma$ to reverse the ordering, while all the other separations contain positive contributions from e_π. For ML$_5$L$'_2$ complexes of pentagonal-bipyramidal geometry (also D_{5h}) it would of course be necessary to use different e_λ parameters for the axial and equatorial ligands, so that again a relationship would be needed, connecting these quantities.

ML$_6$ Systems, Octahedral, O_h. In octahedral symmetry it is well-known[3] that the ligand σ-bonding orbitals transform
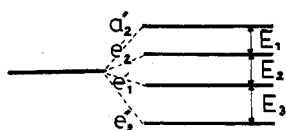
Figure 2. Splitting pattern for f orbitals of ML_7 systems in D_{5h} symmetry. $E_1 = (14e_\sigma - 15e_\pi)/32$, $E_2 = (10e_\sigma + 3e_\pi)/16$, $E_3 = (30e_\sigma + 19e_\pi)/32$.
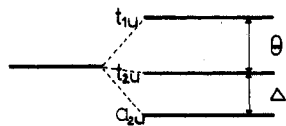

Figure 3. Splitting pattern for f orbitals of ML_6 systems in O_h symmetry. $\theta = 2e_\sigma - e_\pi$, $\Delta = 5\,e_\pi/2$.

as $a_{1g} + e_g + t_{1u}$, and consequently only the t_{1u} f orbitals (z^3 etc.) are σ antibonding. The ligand π orbitals however transform as $t_{1g} + t_{2g} + t_{1u} + t_{2u}$, and although Jorgensen[3] has approximated by ascribing all the f-orbital π bonding ($=4e_\pi$) to the t_{2u} level, it is clear that in principle both the t_{1u} and the t_{2u} ($z(x^2 - y^2)$ etc.) levels may be π antibonding. In fact one finds $E(t_{1u}) - E(t_{2u}) = 2e_\sigma - e_\pi$, and $E(t_{2u}) - E(a_{2u}) = 5e_\pi/2$, so that the a_{2u} level must lie lowest and unless, improbably, $e_\pi > 2e_\sigma$, the t_{1u} level will lie highest.

It is customary[3,13] to represent the one-electron splitting of the octahedral f-orbital set in terms of the parameters θ and Δ, equal respectively to $E(t_{1u}) - E(t_{2u})$, and $E(t_{2u}) - E(a_{2u})$, and these quantities are in turn related to the B_q^k crystal field parameters, as defined by Wybourne,[14] by the expressions $\theta = B_0^4(8/33) + B_0^6(280/429)$ and $\Delta = B_0^4(10/33) - B_0^6(420/429)$. In applications of the angular overlap model[3,15] it has been assumed that the ratio of the e_λ quantities should be equal to the square of the ratio of the corresponding overlap integrals, i.e., $e_\pi/e_\lambda = (S_\pi/S_\sigma)^2$, so that since S_π is frequently about $1/2 S_\sigma$, one anticipates that e_π/e_σ should be of the order of 0.25. For the $5f^2$ systems, $[UCl_6]^{2-}$ and $[UBr_6]^{2-}$, the θ and Δ values quoted by Jorgensen[3] (2640 and 845 cm^{-1} for the former and 2380 and 828 cm^{-1} for the latter) lead to the values $e_\sigma = 1489$ and $e_\pi = 338$ cm^{-1} for $[UCl_6]^{2-}$ and $e_\sigma = 1356$ and $e_\pi = 331$ cm^{-1} for $[UBr_6]^{2-}$, so that $e_\pi/e_\sigma = 0.227$ and 0.244, respectively, in good agreement with the above expectation. However, Schwartz[16] has recently reported a spectroscopic study of the salt $Cs_2NaPrCl_6$, and the crystal field splitting of the ground $^3H_4$ level deduced therefrom may be fitted with the parameters $B_0^4 = 2640$ and $B_0^6 = 147.2$ cm^{-1}, thus leading to $\theta = 736$ and $\Delta = 656$ cm^{-1}, from which are derived the parameters $e_\sigma = 499$ and $e_\pi = 262$ cm^{-1}, with $e_\pi/e_\sigma = 0.525$.

In view of these conflicting results it is fortunate that Brown, Whittaker, and Edelstein[13,17,18] have recently reported the results of studies of the electronic spectra of the $[PaHal_6]^{2-}$ anions (Hal = F, Cl, Br, and I) and have also obtained θ and Δ values both for these systems and for the isoelectronic $5f^1$ species $[UHal_6]^-$, for all of which definitive splitting parameters may much more readily be obtained. In Table IV therefore are listed the θ and Δ parameters for the $[Pa^{IV}Hal_6]^{2-}$ and $[U^VHal_6]^-$ systems, together with the e_σ, e_π, and e_π/e_σ values derived therefrom.

In the two series the relative π-bonding contribution as measured by e_π/e_σ shows a pronounced increase in the sense F < Cl < Br < (I), while for a given halogen the values of this ratio are strikingly similar for the Pa^{IV} and U^V species. As expected both e_σ and e_π are significantly larger in the U^V series than for the Pa^{IV} complexes, due to the greater degree of metal–ligand mixing in the former, but comparison of the Pa^{IV} and U^{IV} hexachloro and hexabromo species shows the e_σ values to be of similar magnitude. The smaller e_π/e_σ values

Table IV. Splitting Parameters for $5f^1$ Systems[a]

Complex	Δ	θ	e_σ	e_π	e_π/e_σ
$[PaF_6]^{2-}$	3074	4502	2866	1230	0.429
$[PaCl_6]^{2-}$	1634	1873	1264	654	0.517
$[PaBr_6]^{2-}$	1707	1268	976	683	0.700
$[PaI_6]^{2-}$	1546	832	725	618	0.852
$[UF_6]^-$	4479	6882	4337	1792	0.413
$[UCl_6]^-$	2936	3371	2273	1174	0.516
$[UBr_6]^-$	2935	2375	1775	1174	0.661

[a] Data from ref 13, 17, and 18; all energies in cm^{-1}.

for the U^{IV} systems thus arise mainly from the low e_π parameters; it is difficult however to decide whether this effect is genuine or if it is due to the strong intermediate coupling in the $5f^2$ systems militating against an accurate determination of all the parameters involved, especially the B_0^4 and B_0^6 quantities which define e_σ and e_π. Thus in the more weakly coupled $4f^2$ system, $[PrCl_6]^{3-}$, the e_π/e_σ ratio of 0.525 is very close to the values found for the chloro complexes of Pa^{IV} and U^V.

Previously it has been suggested[19] that in the hexahalo complexes of the 3d series the magnitude of the splitting parameters, $10Dq$, is largely determined by the σ-bonding contribution, which decreases in the sense F > Cl > Br > I, with a smaller, roughly constant, π-bonding effect. Since the d-orbital set yields only two irreducible representations in O_h symmetry and one splitting parameter, it is not possible to determine e_σ and e_π independently, but the f-orbital set, by yielding three irreducible representations, allows both e_σ and e_π to be evaluated. Thus the $5f^1$ data suggest a situation which differs slightly from that proposed for the 3d complexes; once again the σ-bonding contribution is dominant, decreasing markedly from F to Cl to Br to I, but π bonding, although almost constant for Cl, Br, and I, shows a marked drop between F and Cl. It should however be noted that the values of e_λ depend, as shown by Gerloch and Slade,[5] on no fewer than three parameters—the H^{core} terms of the metal and ligands and the metal–ligand distance; thus trends in the sequences of values obtained for e_σ and e_π for the various halide ligands are not in any simple way related to their electron-donating properties. Clearly though, more spectroscopic data, especially for the $[LnHal_6]^{3-}$ species in the more weakly coupled 4f series, would be of great value in investigating further the relative σ- and π-bonding propensities of the halogen ligands.

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