Theoret. chim. Acta (Berl.) 24, 234—240 (1972)

The Crystal Field Splittings in the 5f Complexes

C. J. BALLHAUSEN*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

Received May 3, 1971

The crystal field splittings of some $(5f)^1$ and $(5f)^2$ complexes are investigated. Octahedral coordination leads to crystal field splittings of the same order of magnitude as the spin-orbit coupling parameter ζ. In contrast to this, tetrahedral coordination produces rather small splittings of the atomic levels. The values of the crystal field parameters Θ and Δ are found to be extremely sensitive to small variations is ζ and render any straight-forward least squares analysis of band positions somewhat dubious. The amount of splitting of the $\Gamma_7 \to \Gamma_8'$ transition provides some insight into the regularity of coordination in $(5f)^1$ compounds. The orders of magnitude for the crystalline field parameters in $(5f)^2$ compounds can distinguish octahedral from tetrahedral coordinations.

Die Kristallfeld-Aufspaltung einiger $5f^1$ und $5f^2$-Komplexe wird untersucht. Oktaedrische Koordination führt zu einer Aufspaltung von etwa der Größenordnung der Spin-Bahn-Kopplungs-Konstanten ζ, während tetraedrische Koordination nur kleine Aufspaltungen der Atomniveaus zur Folge hat. Die Kristallfeldparameter Θ und Δ sind sehr stark von ζ abhängig, weswegen die Adjustierung der drei Parameter an das experimentelle Spektrum recht unsicher wird. Die Aufspaltung des $\Gamma_7 \to \Gamma_8'$-Übergangs trägt zum Verständnis der Koordination in $5f^1$-Komplexen bei. Auf Grund der Größenordnung der Kristallfeldparameter von $5f^2$-Komplexen kann man zwischen tetra- und hexa-Koordination unterscheiden.

Etude des séparations de champ cristallin de certains complexes $(5f)^1$ et $(5f)^2$. Une coordinence octaédrique provoque des séparations de champ cristallin du même ordre de grandeur que le paramètre ζ de couplage spin-orbite. Au contraire, la coordinence tétraédrique produit des séparations de niveaux atomiques plutôt faibles. Les valeurs des paramètres Θ et Δ du champ cristallin sont extrêmement sensibles à de petites variations de ζ, ce qui rend douteux toute analyse directe des positions de bande par la méthode des moindres carrés. L'importance de la séparation de la transition $\Gamma_7 \to \Gamma_8$, fournit certains aperçus sur la régularité de la coordinence dans les composés $(5f)^1$. Les ordres de grandeur des paramètres du champ cristallin dans les composés $(5f)^2$ permet de distinguer les coordinences octaédriques et tétraédrique entre elles.

Introduction

Contrary to the situation for $(4f)^n$ complexes of the rare earths it is usually impossible to treat the "crystalline field" acting on complexes of $(5f)^n$ actinides as a small perturbation of atomic levels. In many cases, the spin-orbit coupling parameter ζ and the crystalline field parameters are of comparable magnitude; as a result, the level diagrams for complexes of the actinides containing more than one $5f$ electron are very complicated. On the other hand, there are also some cases where the "crystalline field" appears to be small compared with ζ. We shall show here that these differences result from the coordination geometry and number of the ion: large crystalline fields corresponding to octahedral coordination, small to tetrahedral coordination.

If we conclude that "crystal field splittings" are *not* due to electrostatic perturbations but reflect, instead, the variations of $\varepsilon^{\text{core}}$ values in a Hartree-Fock

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* Dedicated to the memory of Professor K. H. Hansen.

calculation [1], we must abandon the usual expansion of the crystal field [2] in spherical harmonics. Instead, we must treat the energy separations to be expected from pure symmetry considerations as parameters. Such a treatment focuses attention on the "strong field" point of view that is, with Eisenstein and Pryce [3], the energy matrices will be diagonal in the crystalline field splittings. It is our belief that this approach provides a better understanding of the "crystalline field" than does the eventually equivalent perturbation of the $j-j$ levels [4, 5].

In most cases, the actual symmetry of the complex molecule is very low. We shall, however, neglect this feature and treat the systems as if they possessed high symmetry. This will, of course, preclude any "exact" fitting of the energy levels, but will hopefully concentrate the attention on the important features.

Theory

Consider one f-electron in a regular six-coordination of ligands which possesses O_h symmetry. The seven f-orbitals form a basis for the irreducible representations a_{2u}, t_{1u}, and t_{2u} of O_h. The six sigma ligand orbitals and the twelve pi ligand orbitals can form molecular orbitals with $t_{1u}(\sigma, \pi)$ and with $t_{2u}(\pi)$. Consequently, we expect a splitting pattern as in Fig. 1. With $S = \frac{1}{2}$ transforming like Γ_6 in the double group 0*, the splitting pattern in the strong field case that is with t_{1u}, t_{2u}, and a_{2u} level separations large compared to ζ will be as pictured in Fig. 1 (right). Letting the crystal field go to zero leads to the free ion levels pictured in Fig. 1 (left).

The assumption of a tetrahedral configuration of the ligands changes this splitting pattern drastically. The f-orbitals now transform as a_1 (correlating with a_{2u} in O_h) $t_2(t_{1u}$ in $O_h)$ and $t_1(t_{2u}$ in $O_h)$. The σ ligand orbitals transform as t_2 and a_1, the π ligand orbitals as t_1, t_2, and e. Since the σ group overlap integrals $G(\sigma, a_1) = \frac{2}{3}\sqrt{5}\, S(\sigma, f\sigma)$ and $G(\sigma, t_2) = -\frac{4}{3}\sqrt{3}\, S(\sigma, f\sigma)$, we shall assume $\varepsilon^{\text{core}}(a_1) > \varepsilon^{\text{core}}(t_2) > \varepsilon^{\text{core}}(t_1)$. $S = \frac{1}{2}$ transforms again [6] like Γ_6 and the ensuing splitting pattern is pictured in Fig. 2.

A comparison of Figs. 1 and 2 show that formal reversal of the level order occurs in going from O_h to T_d symmetry. This is, however, a little deceptive; the two t levels are reversed only in name [6].

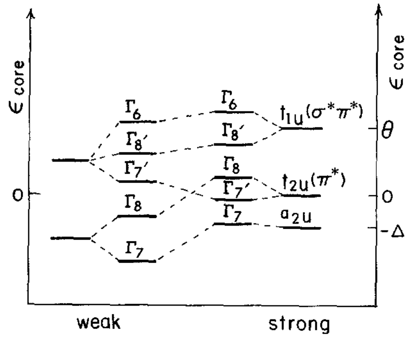

Fig. 1. Crystalline field splitting pattern for fields of O_h symmetry

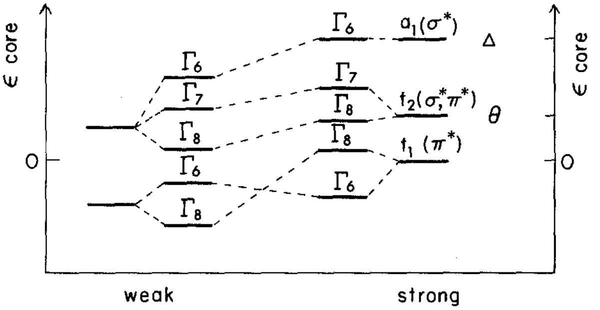

Fig. 2. Crystalline field splitting pattern for fields of T_d symmetry

With Reisfeld and Crosby [5] we shall define $\varepsilon^{\text{core}}(t_{2u}) - \varepsilon^{\text{core}}(a_{2u}) \equiv \Delta$ in O_h symmetry, and similarly $\varepsilon^{\text{core}}(t_1) - \varepsilon^{\text{core}}(a_1) \equiv \Delta$ for T_d symmetry. Notice the similarity of definitions; however, note also that Δ is negative for T_d symmetry and positive for O_h symmetry. We also define $\varepsilon^{\text{core}}(t_{1u}) - \varepsilon^{\text{core}}(t_{2u}) \equiv \Theta$ for O_h symmetry and $\varepsilon^{\text{core}}(t_2) - \varepsilon^{\text{core}}(t_1) = \Theta$ in T_d symmetry. Hence, Θ, as defined here, has the same sign for both tetrahedral and octahedral coordination.

If we adopt the equality $\varepsilon^{\text{core}}(t_{2u}) = \varepsilon^{\text{core}}(t_1) = 0$, we emphasize that the interaction between the levels depends only upon either Θ or Δ. Furthermore, the changes which accompany the transition from octahedral to tetrahedral geometry are easy to visualize.

The octahedral and tetrahedral matrices are then as given by Eisenstein and Pryce [3], but with our change of notation for the crystalline field parameters:

$$\begin{vmatrix} \frac{1}{4}\zeta - \lambda & \frac{3\sqrt{5}}{4}\zeta \\ \frac{3\sqrt{5}}{4}\zeta & \Theta - \frac{3}{4}\zeta - \lambda \end{vmatrix} = 0 \qquad \begin{matrix} O_h\colon \Gamma_8 \\ T_d\colon \Gamma_8, \end{matrix}$$

$$\begin{vmatrix} -\Delta - \lambda & \sqrt{3}\zeta \\ \sqrt{3}\zeta & -\frac{1}{2}\zeta - \lambda \end{vmatrix} = 0 \qquad \begin{matrix} O_h\colon \Gamma_7\ (\Delta \text{ positive}) \\ T_d\colon \Gamma_6\ (\Delta \text{ negative}), \end{matrix}$$

$$\left|\frac{3}{2}\zeta + \Theta - \lambda\right| = 0 \qquad \begin{matrix} O_h\colon \Gamma_6 \\ T_d\colon \Gamma_7 . \end{matrix}$$

In a strong octahedral field, Γ_7' is the first excited level whereas in the week field, Γ_8 drops below Γ_7'. The cross-over occurs when

$$\zeta\left(4\frac{\Delta}{\Theta} + \frac{15}{4}\frac{\Theta}{\Delta} + \frac{17}{2}\right) = \Theta + \Delta .$$

Assuming $\Theta \simeq 2\Delta$ this expression reduces to $\Delta \simeq 6\zeta$. Evidently the cross-over will take place only at quite strong crystalline fields.

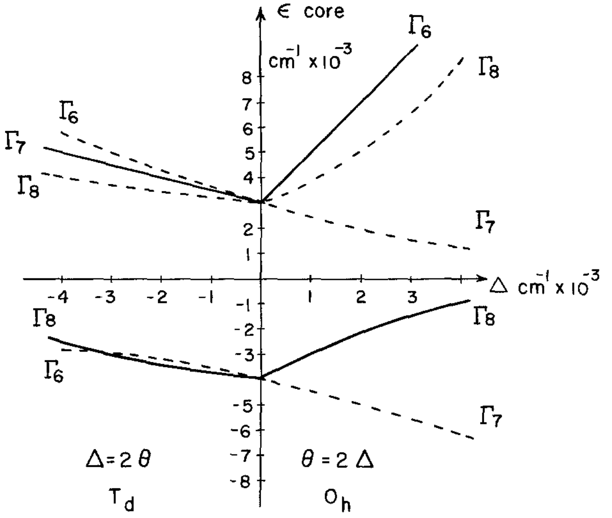

Fig. 3. Quantitative energy diagram for $\varepsilon^{\text{core}}$ in octahedral and tetrahedral fields. Assuming $\zeta = 2000\ \text{cm}^{-1}$ we have in O_h taken $\Theta = 2\Delta$ but in T_d $\Delta = 2\Theta$

Assuming T_d symmetry, the cross-over of Γ_6 and Γ_8 is found when

$$\zeta\left(4\frac{\Delta}{\Theta}+\frac{15}{4}\,\frac{\Theta}{\Delta}-\frac{17}{2}\right)=\Theta-\Delta\,.$$

For $\Delta \simeq 2\Theta$ this implies $\Theta = \frac{11}{8}\zeta$; the crossing takes place in the "intermediate field" region. Evidently the magnetic properties of tetrahedrally coordinated $5f$ complexes are expected to be very different from those which are octahedrally coordinated.

Assuming $\zeta = 2000\ \text{cm}^{-1}$ and $\Theta = 2\Delta$, the splitting pattern to be expected in O_h symmetry is shown in Fig. 3. The same figure also gives the tetrahedral splittings for $|\Delta| = 2\Theta$. It is clear that quite strong tetrahedral fields provide little alteration of the levels of the "naked" ion. The reason relates to the fact that, in tetrahedral geometry one group of six-fold and another group of eight-fold degenerate levels remain bunched together through the whole range of field strengths. In octahedral geometry the two groups do intermix and, as a result, large splittings are produced. To good approximation, tetrahedral complexes of ($5f$) ions can therefore be treated as having a small crystalline field in contrast to the octahedral complexes where the splitting must be considered large. Furthermore, eight coordination in the form of a cube should also produce quite small splittings. A distortion of the octahedron towards D_4 will split Γ_8 into two Kramer's doublets – but the overall "strength" of the crystalline field should remain of the octahedral type.

In O_h symmetry the $\Gamma_7 \to \Gamma_7'$ transition is given by

$$\bar{\nu}(\Gamma_7 \to \Gamma_7') = \sqrt{\left(\Delta - \frac{1}{2}\zeta\right)^2 + 12\zeta^2}\,.$$

For $\Delta \leqq \zeta$ we can expand:

$$\bar{\nu}(\Gamma_7 \to \Gamma_7') \simeq \frac{7}{2}\zeta + \frac{\Delta(\Delta-\zeta)}{7\zeta} \approx \frac{7}{2}\zeta .$$

In other words this transition should occur at $\sim\frac{7}{2}\zeta$ and should be more or less independent of Δ. Taking the experimental value for $\bar{\nu}(\Gamma_7 \to \Gamma_7')$ as a constant, the permitted variations of Δ and ζ are given by $(2\Delta-\zeta)\,\delta\Delta = (\Delta - \frac{49}{2}\zeta)\,\delta\zeta$. With $\Delta \simeq \zeta$, this reduces to $\delta\Delta = -23.5\,\delta\zeta$. In other words a change in the value of ζ by $40\,\mathrm{cm}^{-1}$ will change the value of the parameter Δ by $1000\,\mathrm{cm}^{-1}$. Hence the parameter Δ is very poorly determined and it is extremely sensitive to the value of ζ.

The three experimentally observed transitions in octahedrally coordinated U^{+5} complexes are $\Gamma_7 \to \Gamma_7'$, $\Gamma_7 \to \Gamma_8'$ and $\Gamma_7 \to \Gamma_6$. In principle, it should be possible to evaluate the three parameters Δ, Θ and ζ using a least square analysis. However, the very strong dependence of Δ and Θ upon ζ makes such a procedure dubious. Furthermore, the degeneracy intrinsic to the $\Gamma_7 \to \Gamma_8'$ transition is usually removed by deviations from the idealized octahedral field. These deviations in turn introduce three additional splitting parameters which must be evaluated simultaneously with Δ, Θ and ζ. It is quite clear that even though an excellent understanding of the spectrum can be generated we cannot expect to extract a unique parametric set which is precisely descriptive of band positions. Such a parameter set is therefore not neccessarily physical meaningful. The parameter values given in Table 2, are therefore not the only possible sets, they are merely representative. In our assignments we follow Selbin *et al.* [11] and Karraker [12] rather than Reisfeld and Crosby [5] who did not recognize the splitting of the $\Gamma_7 \to \Gamma_8'$ transitions.

Table 1. Values from a Hartree-Fock calculations of ζ_{5f} for some $(5f)^1$ systems [8]

Pa^{+4} : $\zeta_{5f} = 1584\,\mathrm{cm}^{-1}$
U^{+5} : $\zeta_{5f} = 2063\,\mathrm{cm}^{-1}$
Np^{+6} : $\zeta_{5f} = 2553\,\mathrm{cm}^{-1}$

Table 2. Parameter values for some $(5f)^1$ complexes

$\mathrm{PaCl}_6^{=}$	$\Gamma_7 \to \Gamma_7'$	$\Gamma_7 \to \Gamma_8'$	$\Gamma_7 \to \Gamma_6$
Ref. [9]	$5215\,\mathrm{cm}^{-1}$	$7085\,\mathrm{cm}^{-1}$	$8000\,\mathrm{cm}^{-1}$
Parameters	$\zeta = 1500\,\mathrm{cm}^{-1}$	$\Delta = 1500\,\mathrm{cm}^{-1}$	$\Theta = 2000\,\mathrm{cm}^{-1}$
$\mathrm{UCl}_6^{=}$	$\Gamma_7 \to \Gamma_7'$	$\Gamma_7 \to \Gamma_8'$	$\Gamma_7 \to \Gamma_6$
Ref. [7]	$6800\,\mathrm{cm}^{-1}$	$9950\,\mathrm{cm}^{-1}$ $10430\,\mathrm{cm}^{-1}$	$11470\,\mathrm{cm}^{-1}$
Parameters	$\zeta = 1940\,\mathrm{cm}^{-1}$	$\Delta = 1940\,\mathrm{cm}^{-1}$	$\Theta = 3710\,\mathrm{cm}^{-1}$
NpF_6	$\Gamma_7 \to \Gamma_8$	$\Gamma_7 \to \Gamma_7'$	$\Gamma_7 \to \Gamma_8'$
Ref. [10]	$7540\,\mathrm{cm}^{-1}$	$9350\,\mathrm{cm}^{-1}$	$(24000\,\mathrm{cm}^{-1})$
Parameters[a]	$\zeta = 2400\,\mathrm{cm}^{-1}$	$\Delta = 5440\,\mathrm{cm}^{-1}$	$\Theta = 16800\,\mathrm{cm}^{-1}$

[a] The transitions found around $4000\,\mathrm{cm}^{-1}$ cannot be electronic in origin. See also Ref. [3].

Discussion and Conclusions

The $\Gamma_7 \rightarrow \Gamma_8'$ transition is often quite strongly split, and the amount of this splitting serves as indicator for deviations from octahedral symmetry. An illustrative calculation [13] of the effects of the introduction of lower fields indicates that the position of $\Gamma_7 \rightarrow \Gamma_7'$ should remain more or less unaltered, that $\Gamma_7 \rightarrow \Gamma_8'$ and $\Gamma_7' \rightarrow \Gamma_8$ should split significantly and that $\Gamma_7 \rightarrow \Gamma_6$ should tend toward higher energies. These expectations are certainly fulfilled [7, 13].

Of some interest here is the spectrum of the gaseous dimer U_2Cl_{10} reported by Gruen and McBeth [14]. $\Gamma_7 \rightarrow \Gamma_7$ is found at 6660 cm^{-1}, almost as in UCl_6^-, and the components of Γ_8' are split by ~ 800 cm^{-1}. Since the low energy $\Gamma_7 \rightarrow \Gamma_8$ transition should be strongly split it is reasonable to infer that the band observed at 4500 cm^{-1} corresponds to the upper energy component of Γ_8.

No tetrahedral $(5f)^1$ systems seem to have been characterized. However, when interpreting the spectrum of the $(5f)^2$ compound UCl_4, McLaughlin [15] commented that the spectrum was virtually identical to that expected for the free ion. The structure is known to be an extremely flattened tetrahedron. Later measurements on UCl_4 by Clifton, Gruen and Ron [16] yielded (as recalculated here) $\Delta = -1100$ cm^{-1} and $\Theta = -1130$ cm^{-1}. However, the values of these parameters were obtained by a least-squares fit which assumed a regular tetrahedral coordination and which maintained the values of F_2, F_4, F_6 and ζ_{5f} constant, the last being set equal to 1796 cm^{-1}. Hence all we can safely conclude is that Δ is fairly small and negative. For $UCl_6^=$ in Cs_2UCl_6 where U^{+4} is found at an O_h site, Satten, Schreiber, and Wong [17] found (as recalculated here) $\Delta = 1330$ cm^{-1} and $\Theta = 2370$ cm^{-1}. These values were obtained from a least square fit to 18 observed levels, which provide an evaluation of 6 parameters, including $\zeta_{5f} = 1796$ cm^{-1}.

The spectrum of $CsNpF_6$ was interpreted by Varga *et al.* [8] assuming octahedral coordination. Thirty four observed levels were used in a least-squares refinement of the crystal field parameters. If ζ_{5f} is maintained constant at 2380 cm^{-1} one finds (recalculated here) $\Delta = 375$ cm^{-1} and $\Theta = 1080$ cm^{-1}. If ζ is allowed to vary one finds $\zeta_{5f} = 2230$ cm^{-1}, $\Delta = -210$ cm^{-1} and $\Theta = 610$ cm^{-1}. We must conclude from these parameter values that Np^{+5} is not octahedrally coordinated. We suspect a flattened tetrahedral geometry.

Therefore it would appear possible to infer some structural conclusions from the parametric values necessitated by a formal crystalline field description of the spectra of $(5f)^2$ complexes.

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Prof. C. J. Ballhausen
Dept. of Chemistry
Louisiana State University
Baton Rouge, Louisiana 70803, USA