it is not an excited-state association reaction as originally suggested.[1] All attempts to develop a photochromic system which could be repeatedly cycled have failed.

Experimental Section

Methyl isocyanide,[13] *tert*-butyl isocyanide,[14] and $[IrCl(1,5\text{-cyclooctadiene})]_2$[15] were prepared by published procedures, and solvents were purified by standard methods. All experiments and manipulations of compounds were conducted under vacuum or under a purified N_2 atmosphere.

Preparation of $[Ir(CNCH_3)_4]Cl$ and $[Ir(CN\text{-}t\text{-}Bu)_4]Cl$. Excess CH_3NC was distilled into a Schlenk tube containing $[IrCl(1,5\text{-cyclooctadiene})]_2$ (0.30 g; 0.4 mmol) in 20 mL of CH_2Cl_2, and the mixture was stirred for 1 h. The solvent, excess $CNCH_3$, and 1,5-cyclooctadiene were removed under vacuum. The crude product was dissolved in methanol and filtered. Evaporation of solvent gave a blue-black solid. Other salts were prepared by metathesis in methanol using $NaBPh_4$ and $NaBF_4$. $[Ir(CN\text{-}t\text{-}Bu)_4]Cl$ was obtained as an orange solid by an exactly analogous procedure using excess *tert*-butyl isocyanide.

General Irradiation Procedures. Irradiations were conducted using a 450-W Hanovia medium-pressure Hg lamp in a quartz well equipped with one of the following Corning glass filters: 5-74 (λ 436 nm); 7-83 (λ 366 nm); 3-70 ($\lambda \geq 525$ nm). The complex to be studied was placed in an degassable quartz UV cell or a Schlenk tube, and after degassing on a vacuum line, the appropriate solvent was distilled onto the sample. Solutions for infrared studies were transferred in an inert-atmosphere glovebox to 0.5-mm NaCl-solution infrared cells. Lamp intensities were measured using ferrioxalate actinometry[16] and were of the order of 4.0×10^{-7} einstein/min (436 nm).

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Registry No. $[Ir(CNCH_3)_4]Cl$, 40226-52-6; $[Ir(CN\text{-}t\text{-}Bu)_4]Cl$, 34389-90-7; $[IrCl(1,5\text{-cyclooctadiene})]_2$, 12112-67-3.

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Correspondence

Reinvestigation of the Coordination Geometry of Eight-Coordinate Metal Tetrakis(acetylacetonates)

Sir:

Although several sets of parameters have been devised to measure the shape of a discrete eight-coordinate complex with reference to idealized geometric forms,[1-4] some confusion still exists in the assignment of an idealized geometry to an observed eight-coordinate complex. A case in point is the series of acetylacetonate (acac) complexes with actinides, lanthanides, and group 4B elements. The individual eight-coordinate tetrakis(acetylacetonate) complexes exist in either of two crystalline modifications (the α and β forms); the coordination geometry of the β form has been described as primarily square antiprismatic,[5-8] while that of the α form has been described as predominantly dodecahedral[9,10] and as predominantly antiprismatic.[11]

We have reexamined the tetrakis(acetylacetonate) series by calculating the ϕ and δ shape parameters[3,4,12] for α-Ce(acac)$_4$, α-Th(acac)$_4$, β-Zr(acac)$_4$, β-Ce(acac)$_4$, β-U(acac)$_4$, and β-Np(acac)$_4$. The results are given in Table I. The results of mean-planes calculations, assuming both dodecahedral and antiprismatic geometries for both series of complexes, are listed in Table II. Tables III and IV give the atomic coordinates and the definition of the planes used in the calculation of the shape parameters for the α and β forms, respectively.

Table I. Shape Parameters (deg) for M(acac)$_4$ Complexes[a]

Compd	ϕ_1	ϕ_2	δ_1	δ_2	δ_3	δ_4
D_{2d} dodecahedron[b]	0.0	0.0	29.5	29.5	29.5	29.5
C_{2v} bicapped trigonal prism[b]	14.1	14.1	0.0	21.8	48.2	48.2
D_{4d} square antiprism[b]	24.5	24.5	0.0	0.0	52.4	52.4
α-Ce(acac)$_4$	12.8	15.3	9.7	21.1	44.0	42.9
α-Th(acac)$_4$	15.6	17.3	5.4	19.8	44.5	44.9
β-Zr(acac)$_4$	22.8	22.4	3.2	3.2	49.6	49.6
β-Ce(acac)$_4$	19.7	19.3	5.3	5.3	46.7	46.7
β-U(acac)$_4$	22.1	17.8	6.8	6.8	49.2	49.2
β-Np(acac)$_4$	22.3	20.6	4.5	4.5	50.5	50.5

[a] The planes defining the ϕ and δ angles are given for the α complexes in Table III and for the β complexes in Table IV.
[b] Values of the shape parameters for the idealized geometries were taken from ref 4.

The idealized geometry most closely approximated by the coordination groups of α-Ce(acac)$_4$ and α-Th(acac)$_4$ is neither the D_{2d} dodecahedron nor the D_{4d} square antiprism but rather the C_{2v} bicapped trigonal prism, as shown by the shape parameters in Table I. The assignment of primarily dodecahedral geometry to the coordination group of the α complexes by Allard[9] was based on a comparison of observed normalized polyhedral edge lengths with the corresponding edge lengths for the "most favorable polyhedra".[1] However, it is very difficult on this basis to assign an idealized geometry to the α complexes since their edge lengths are approximately midway between those of the dodecahedron and the square antiprism. If anything, there appears to be a slight tendency toward antiprismatic coordination. Our calculation of the ϕ and δ shape parameters assigns the geometry of the α complexes as quite close to bicapped trigonal prismatic. Moreover, since the bicapped trigonal prism is along the reaction pathway between the dodecahedron and square antiprism,[3,4] our calculation is in quite good agreement with the polyhedral edge lengths given by Allard.

The mean-planes calculations for α-Ce(acac)$_4$ and α-Th(acac)$_4$ (see Table II) show a large degree of nonplanarity for the BAAB trapezoids, again indicating that the α complexes do not closely approximate dodecahedral geometry. One of the square faces for the antiprismatic model is also relatively nonplanar. Note, however, that the deviations of the atoms from the plane of the other square face, the face corresponding

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Table II. Mean Planes for M(acac)$_4$ Complexes

Compd	BAAB trapezoids Plane 1	BAAB trapezoids Plane 2	Square faces[a] Plane 1	Square faces[a] Plane 2	Dihedral angle between trapezoids, deg	Dihedral angle between square faces, deg
α-Ce(acac)$_4$	0.141[b]	−0.172[b]	0.086[b]	0.186[b]	88.6	1.6
	−0.224	0.269	−0.084	−0.189		
	0.224	−0.266	0.083	0.193		
	−0.141	0.169	−0.085	−0.190		
α-Th(acac)$_4$	0.167	−0.202	0.047	0.180	90.0	1.1
	−0.270	0.312	−0.048	−0.183		
	0.287	−0.304	0.049	0.182		
	−0.184	0.194	−0.047	−0.179		
β-Zr(acac)$_4$	−0.236	0.234	0.027		84.1	0.0
	0.376	−0.367	−0.027			
	−0.376	0.367	−0.027			
	0.236	−0.234	0.027			
β-Ce(acac)$_4$	−0.229	−0.222	0.046		85.5	0.6
	0.345	0.344	−0.046			
	−0.345	−0.344	−0.046			
	0.229	0.222	0.046			
β-U(acac)$_4$	−0.259	−0.193	0.057		85.1	3.5
	0.398	0.310	−0.057			
	−0.398	−0.310	−0.060			
	0.259	0.193	0.060			
β-Np(acac)$_4$	−0.245	−0.232	0.038		83.4	0.0
	0.396	0.358	−0.037			
	−0.396	−0.358	−0.039			
	0.245	0.232	0.038			

[a] In the β crystalline form the two square faces are rendered equivalent by a crystallographic twofold axis. [b] The numbers given are the displacements (A) of the individual atoms from the planes defined in Tables III and IV.

Table III. Atomic Coordinates[a] and Shape Parameter Definitions for α-M(acac)$_4$ Complexes

Atom	x	y	z
Th	0.1903	0.1464	0.2003
O_1	0.0618	0.1791	0.0562
O_2	0.0398	0.0150	0.1535
O_3	0.2108	0.3323	0.2005
O_4	0.0098	0.2219	0.2061
O_5	0.1888	0.1200	0.3379
O_6	0.3885	0.1914	0.3011
O_7	0.3010	−0.0141	0.2275
O_8	0.3297	0.1361	0.1256

Shape parameter[b]	Plane 1	Plane 2
ϕ_1	$O_5M_{14}{}^cO_8$	$O_1M_{58}{}^cO_4$
ϕ_2	$O_2M_{67}{}^cO_3$	$O_6M_{23}{}^cO_7$
δ_1	$O_1O_2O_8$	$O_2O_7O_8$
δ_2	$O_3O_4O_5$	$O_3O_5O_6$
δ_3	$O_1O_3O_8$	$O_3O_6O_8$
δ_4	$O_2O_4O_5$	$O_2O_5O_7$
BAAB trapezoids[d]	$O_8O_1O_4O_5$	$O_3O_6O_7O_2$
Square faces	$O_1O_2O_7O_8$	$O_3O_4O_5O_6$

[a] The fractional atomic coordinates used in the calculations were taken from ref 10 and 11. The coordinates shown are those for α-Th(acac)$_4$. [b] The ϕ and δ parameters are dihedral angles between plane 1 and plane 2. [c] M_{xy} refers to the midpoint between oxygen atoms x and y. [d] The trapezoids given are those for the *gggg* stereoisomer.

to the noncapped square face of the bicapped trigonal prism, are rather small.

A view of the coordination group in α-Th(acac)$_4$ emphasizing its bicapped-trigonal-prismatic nature is shown in Figure 1, and a view down the pseudo-threefold axis of the trigonal prism is presented in Figure 2. Figure 3 shows the ligand wrapping pattern for α-Th(acac)$_4$. Oxygen atoms 1, 3, and 8 and 2, 5, and 7 form the triangular faces of the trigonal prism; oxygen atoms 4 and 6 cap two of the three quadrilateral

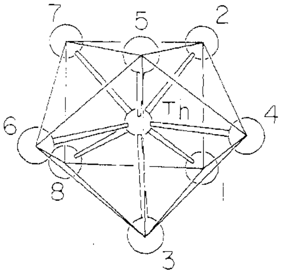

Figure 1. A view (ORTEP) of the coordination group of α-Th(acac)$_4$ showing its bicapped trigonal prismatic shape.

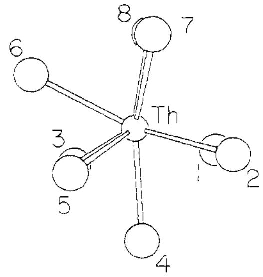

Figure 2. A view (ORTEP) down the pseudo-threefold axis of the coordination group of α-Th(acac)$_4$.

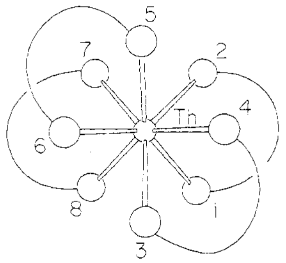

Figure 3. A view (ORTEP) down the pseudo-$\bar{8}$ axis of α-Th(acac)$_4$.

Table IV. Atomic Coordinates[a] and Shape Parameter Definitions for β-M(acac)$_4$ Complexes

Atom	*x*	*y*	*z*
Np	0.0000	−0.0676	0.2500
O_1	0.0623	−0.2821	0.2410
O_2	0.1121	0.0186	0.3025
O_3	0.0507	−0.1548	0.4175
O_4	0.0089	0.1426	0.3551
O_1'	−0.0623	−0.2821	0.2590
O_2'	−0.1121	0.0186	0.1975
O_3'	−0.0507	−0.1548	0.0825
O_4'	−0.0089	0.1426	0.1449

Shape parameter[b]	Plane 1	Plane 2
ϕ_1	$O_2M_{11'}$, $^cO_2'$	$O_1M_{22'}$, $^cO_1'$
ϕ_2	$O_3M_{44'}$, $^cO_3'$	$O_4M_{33'}$, $^cO_4'$
δ_1	$O_3O_1'O_2'$	$O_3O_4O_2'$
δ_2	$O_1O_2O_3'$	$O_2O_3'O_4'$
δ_3	$O_1'O_2'O_3'$	$O_2'O_3'O_4'$
δ_4	$O_1O_2O_3$	$O_2O_3O_4$
BAAB trapezoids[d]	$O_2'O_1'O_1O_2$	$O_3'O_4'O_4O_3$
Square faces	$O_1O_2O_3'O_4'$	*e*

[a] The fractional atomic coordinates used in the calculations were taken from ref 5–8. The coordinates shown are those for β-Np(acac)$_4$. [b] The ϕ and δ parameters are dihedral angles between plane 1 and plane 2. [c] M_{xy} refers to the midpoint between oxygen atoms *x* and *y*. [d] The trapezoids given are those for the *mmmm* stereoisomer. [e] The two square faces are rendered equivalent by a crystallographic twofold axis.

Table V. Polyhedral Edge Lengths for α-M(acac)$_4$ Complexes

			Length, A			
Edge[a]	Atoms		α-Ce(acac)$_4$		α-Th(acac)$_4$	
t_1	O_2–O_7	O_1–O_8	2.803	2.736	2.871	2.970
t_2	O_2–O_5	O_3–O_8	3.239	3.251	3.253	3.352
	O_5–O_7	O_1–O_3	3.009	2.991	3.179	3.114
p_1	O_4–O_2	O_6–O_8	2.747	2.883	2.859	2.891
	O_4–O_1	O_6–O_7	2.817	2.847	2.895	2.927
p_2	O_4–O_5	O_6–O_3	2.743	2.775	2.757	2.801
	O_4–O_3	O_6–O_5	2.790	2.731	2.787	2.805
h_1	O_1–O_2	O_7–O_8	2.713	2.731	2.747	2.695
h_2	O_3–O_5		3.656		3.658	

[a] See Figure 1 and ref 3 for a definition of edge nomenclature.

faces. The observed ligand wrapping pattern for the α-M(acac)$_4$ complexes gives the $h_1h_1p_2p_2$ stereoisomer of the bicapped trigonal prism according to the notation of Porai-Koshits and Aslanov.[3,13] The $h_1h_1p_2p_2$ stereoisomer lies along the deformation pathway between the *ssss* square antiprismatic stereoisomer and the *gggg* dodecahedral stereoisomer. If the *ssss* stereoisomer (see Figure 3) is taken as the starting point, then a folding of one square face about the O_3O_5 diagonal and a slight shortening of the O_3O_5 diagonal produce the observed $h_1h_1p_2p_2$ bicapped trigonal prismatic stereoisomer. A folding about and slight shortening of the O_2O_8 diagonal of the remaining square face would then lead to the *gggg* dodecahedral stereoisomer. It is therefore easy to understand how the coordination geometry of the α-M(acac)$_4$ complexes could have been interpreted as *ssss* antiprismatic or *gggg* dodecahedral.

The polyhedral edge lengths for α-Ce(acac)$_4$ and α-Th(acac)$_4$ are listed in Table V. There are some significant deviations from the edge lengths of the idealized bicapped trigonal prism based on the hard-sphere model. For example, the two types of edges (t_1 and t_2) which define the triangular faces of the trigonal prism differ in length, and the longer t_2 edges are also longer than the edges (p_1 and p_2) which terminate at the capping atoms; all four edges (t_1, t_2, p_1, and p_2) are required to be identical in the hard-sphere model. The p_1 and p_2 edges are, however, remarkably uniform with an average length of 2.792 Å and a range of 2.731–2.883 Å for the Ce complex and an average length of 2.840 Å and a range of 2.757–2.927 Å for the Th complex. Thus, the capping atoms are very nearly centered on the quadrilateral faces. The O_1O_2 and O_7O_8 edges (h_1) are spanned by the bidentate acetylacetonate ligands and are therefore much shorter than the O_3O_5 edge (h_2). The two triangular faces of the trigonal prism are thus nonparallel (dihedral angle, 19.1° for α-Ce(acac)$_4$ and 18.7° for α-Th(acac)$_4$), and the capped faces are trapezoidal rather than rectangular.

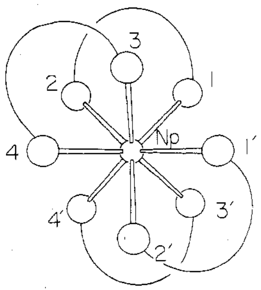

Figure 4. A view (ORTEP) down the pseudo-$\bar{8}$ axis of β-Np(acac)$_4$. The primed and unprimed oxygen atoms are related by a crystallographic twofold axis.

A comparison of Figures 1–3 and the view of an α-M(acac)$_4$ complex given by Allard[9] shows that computer-drawn molecular diagrams can sometimes be misleading. In the view given in Allard's paper the molecule of α-M(acac)$_4$ appears to approximate dodecahedral geometry while in the view shown in Figure 3 it appears to closely approximate square-antiprismatic geometry. However, our calculations, as discussed above, indicate that the α-M(acac)$_4$ complexes most closely approximate bicapped-trigonal-prismatic geometry, as shown in Figures 1 and 2. Therefore, when a series of possible geometries are closely related and lie along a reaction pathway, such as in the case of eight-coordination, tabulations of δ and ϕ shape parameters, mean planes, polyhedral edge lengths, and interbond angles should be given in conjunction with the chosen view to accurately depict the geometry of the complex.

The assignment of square-antiprismatic geometry to the β-M(acac)$_4$ complexes is unambiguous. Our calculation of the δ and ϕ shape parameters (see Table I), as well as Allard's listing of edge lengths, indicates that the square antiprism is the idealized geometry closest to that of the β-M(acac)$_4$ complexes. The slight distortions from idealized square-antiprismatic geometry involve folding (see Figure 4) about the O_3O_2' and O_2O_3' diagonals, distortions in the direction of the *mmmm* dodecahedral stereoisomer.[5,9]

A further example of ambiguity in the assignment of coordination geometry involves tetrakis(*N*,*N*-diethyldithiocarbamato)thorium(IV), Th(Et$_2$dtc)$_4$, an eight-coordinate complex whose geometry has been described as intermediate between dodecahedral and square antiprismatic.[14] The assignment of intermediate geometry was based on a calculation of θ_A and θ_B, where θ_A and θ_B are the angles which the M–A and M–B bonds make with the $\bar{4}$ axis of the D_{2d} dodecahedron or with the $\bar{8}$ axis of the D_{4d} square antiprism.[1] The values for the "most favorable polyhedra" are $\theta_A = 35.2°$ and $\theta_B = 73.5°$ for the dodecahedron and $\theta_A = \theta_B = 57.3°$ for the square antiprism.[1] The reported values of $\theta_A = 44°$ and $\theta_B = 66°$ for the thorium complex[14] are, however, the angles which the M–A and M–B bonds make with a crystallographic twofold axis which is *not* coincident with the $\bar{4}$ axis of the dodecahedron but rather perpendicular to it. A calculation of the angles which the M–A and M–B bonds make with the $\bar{4}$ axis of the dodecahedron (taken as the line passing through the midpoints of the two *a* edges and through the thorium atom) yields values of 34.8° for θ_A and 83.0° for θ_B. Thus, Th(Et$_2$dtc)$_4$ is apparently much closer to dodecahedral (*mmmm* stereoisomer) than to square-antiprismatic geometry. A determination of the δ and ϕ shape parameters for Th(Et$_2$dtc)$_4$ confirms its approximation to dodecahedral geometry; the δ parameters are 31.4, 33.5, 41.9, and 41.9° and the one unique ϕ value is 5.1°. (See Table I for a listing of the δ and ϕ parameters for the idealized dodecahedron and square antiprism.) The dihedral angle between the interpenetrating BAAB trapezoids of the dodecahedron is 89.6°, with the four sulfur atoms which define an individual trapezoid being planar to within 0.11 Å.

The cases of misdescription of coordination geometry discussed above emphasize that the idealized eight-coordinate geometries are closely related by fairly small deformations along a reaction pathway and that assignment of one of the idealized geometries to an observed complex should be based on an analysis of more than one set of shape parameters. Although calculations of the θ_A and θ_B angles and of normalized edge lengths are often very useful in describing the geometry of a complex, a tabulation of δ and ϕ shape parameters, as well as results of appropriate mean-planes calculations, should be provided in defense of an assigned geometry. In addition, in cases of tetrakis complexes with bidentate chelating ligands, the ligand wrapping pattern should be identified. A clear and convincing description of the geometry of an observed complex can thus be given.

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Registry No. α-Ce(acac)$_4$, 65137-07-7; α-Th(acac)$_4$, 65137-06-6; β-Zr(acac)$_4$, 65137-05-5; β-Ce(acac)$_4$, 65137-04-4; β-U(acac)$_4$, 65137-03-3; β-Np(acac)$_4$, 65137-02-2.

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(12) The four δ shape parameters are the dihedral angles between the pairs of triangular faces which join along the four b edges of the reference D_{2d} dodecahedron. These four dihedral angles are chosen as a criterion of shape because they are more sensitive to polyhedral shape than the dihedral angles between triangular faces which join along the a, m, and g edges of the reference dodecahedron. Upon conversion to the D_{4d} square antiprism, a pair of opposite dodecahedral b edges become diagonals of the square faces of the antiprism, and the corresponding δ values decrease from 29.5° in the idealized dodecahedron to 0.0° in the idealized square antiprism; the other two dodecahedral b edges become l edges of the antiprism and the corresponding δ values increase to 52.4° (see Table I). The C_{2v} bicapped trigonal prism has one square face and one δ value equal to 0.0°. Identification of the shape-determining edges (b edges of the reference dodecahedron) is discussed in ref 4.

(13) It is interesting to note that Porai-Koshits and Aslanov excluded from consideration as a "main isomer" the $h_1h_1p_2p_2$ bicapped trigonal prism for complexes with four identical bidentate ligands, on the basis of the difficulty of identical ligands spanning edges which have different lengths in the idealized hard-sphere polyhedron.

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