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Stereochemistry of Transition-Metal Eight-Coordination: The Structure of Tetrakis(*N*-Benzoyl-*N*-phenylhydroxylaminato)hafnium(IV)

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Within the scope of a systematic study of eight-coordinate Hf^{IV} chelates, the structure of tetrakis(*N*-benzoyl-*N*-phenylhydroxylaminato)hafnium(IV), $Hf(NBPHA)_4$, has been determined by single-crystal X-ray diffraction analysis. This compound crystallizes in space group $P\bar{1}$ of the triclinic system, with two formula units per unit cell. The dimensions of the unit cell are $a = 13{\cdot}363$ (2), $b = 13{\cdot}132$ (2), $c = 13{\cdot}015$ (2) Å, $\alpha = 93{\cdot}66$ (1), $\beta = 94{\cdot}12$ (1), $\gamma = 83{\cdot}88$ (1)°. The structure was solved with 6732 independent reflections by the heavy-atom method, and refined to an R factor of 4·6% by block-diagonal-matrix approximation. The HfO_8 coordination group is a strongly distorted dodecahedron. The eight edges, g, of this polyhedron are divided into two classes, g_1 and g_2, with different lengths. The four bidentate NBPHA ligands span the four shorter edges, g_1, in such a way that O atoms of CO and NO groups occupy the coordination sites of types X^A and X^B respectively. The value of the bond-length ratio $Hf–O^A/Hf–O^B$ is unusually high (1·07). This d^0 complex may be considered as an example of a dodecahedral $M(AA')_4$ system whose stereochemistry can be rationalized in terms of ligand–ligand repulsions and metal—ligand π bonding (Orgel's rule).

Introduction

Despite extensive investigations into the stereochemistry of eight-coordinate systems, any anticipation of the geometry adopted by a given eight-coordinate complex remains very difficult. The only stereochemical rule concerning eight-coordination chemistry was formulated by Orgel (1960) who suggested that molecules of the type MX_4Y_4 (M = a d^0, d^1 or d^2 metal ion; X, Y = a monodentate ligand) should adopt dodecahedral stereochemistry. For a given configuration of the central metal ion, the distribution of the ligands among the coordination sites would be determined by their relative π-donor capabilities. The previously reported structures of dodecahedral $M(AB)_4$ chelates having asymmetric bidentate ligands, such as tetrakis(*N*-ethylsalicylideneiminato)zirconium(IV) (Bradley, Hursthouse & Rendall, 1970), tetrakis(8-quinolinato)zirconium(IV) (Lewis & Fay, 1974) and tetrakis(5-bromo-8-quinolinato)tungsten(IV) (Bonds, Archer & Hamilton, 1971), have been shown to verify Orgel's suggestion for d^0 and d^2 complexes.

Orgel's rule cannot be used to predict the stereochemistry of eight-coordinate species such as MX_8 monodentate complexes or ML_4 chelates having chemically symmetric bidentate ligands. However, metal—ligand π bonding can be reasonably expected to contribute significantly to the stability of the molecular structure in these systems.

In order to gain new insight into the structural and electronic properties of eight-coordinate d^0 complexes, a systematic study of Hf^{IV} chelates by both X-ray diffraction experiments and electric-field-gradient tensor measurements (Boyer, Tissier, Vargas & Vulliet, 1972) has been undertaken in our laboratory. Within the scope of this study, we present here the structure of tetrakis(*N*-benzoyl-*N*-phenylhydroxylaminato)-hafnium(VI) [$Hf(NBPHA)_4$ in the following]. This work follows the structure determinations of tetrakis-(tropolonato)hafnium(IV) (Tranqui, Tissier, Laugier & Boyer, 1977) and tetrapotassium tetrakis(oxalato)-hafniate(IV) pentahydrate (Tranqui, Boyer, Laugier & Vulliet, 1977) recently published by our group.

Sample preparation

The $Hf(NBPHA)_4$ chelate was prepared according to the method described by Ryan (1960). The fine white microcrystalline powder thus obtained was then dissolved in methylene chloride up to a concentration of about 150 g l^{-1}. Crystals of suitable dimensions were grown by adding acetone in a ratio of 5/1 and then by evaporating the solution at room temperature for about

Table 1. *Crystal data*

Compound formula: $Hf[(ONC_6H_5)(OCC_6H_5)]_4$
Space group $P\bar{1}$, $Z = 2$
Unit-cell parameters:
$a = 13{\cdot}363 \pm 0{\cdot}002$, $b = 13{\cdot}132 \pm 0{\cdot}002$, $c = 13{\cdot}015 \pm 0{\cdot}002$ Å
$\alpha = 93{\cdot}66 \pm 0{\cdot}01$, $\beta = 94{\cdot}12 \pm 0{\cdot}01$, $\gamma = 83{\cdot}88 \pm 0{\cdot}01°$
$V = 2261$ Å^3

Table 2. *Experimental conditions*

Measurement by ω scanning
Scan width: $A = 1{\cdot}1°$, $B = 0{\cdot}3°$; $\Delta\omega = (A + B\,\mathrm{tg}\,\theta)°$
θ range: $3° \le \theta \le 45{\cdot}2°$
Radiation wavelength: λ(Mo $K\bar{\alpha}$) = 0·7103 Å
Graphite-crystal monochromator

two weeks. For the X-ray diffraction measurements, a selected crystal was conveniently shaped by grinding.

Experimental

A spherical (r = 0·015 cm) crystal of $Hf(NBPHA)_4$ was mounted on an automatic Rigaku-Denki four-circle diffractometer equipped with a 12 kW rotating anode. The dimensions of the unit cell were determined by the automatic investigation of reflection settings. $Hf(NBPHA)_4$ was found to crystallize in the triclinic system; the space group, first assumed to be $P\bar{1}$, was confirmed by the successful refinement of the structure. Crystal data and experimental conditions for intensity-data collection are listed in Tables 1 and 2 respectively. 6732 independent reflections were recorded in about two days. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was made because of the low μr value.

Determination of the structure

The structure of $Hf(NBPHA)_4$ was solved by the heavy-atom method. The calculated three-dimensional Patterson function clearly showed the Hf–Hf vector. More accurate Hf coordinates were then obtained by least-squares calculations. All the other nonhydrogen atoms were located by successive Fourier difference syntheses and refinements.

The positional and thermal parameters were definitively obtained after several cycles of least-squares refinements. Owing to the high number (586) of independent parameters which determine the molecular structure, the block-diagonal-matrix approximation was used. The final weighted residual, conventionally defined as $R_w = [\Sigma\, w(|F_o| - k|F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}$, was 4·6%. Atomic coordinates, with their respective standard deviations in parentheses, are given in Table 3.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33029 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Final fractional atomic coordinates of* $Hf(NBPHA)_4$ ($\times 10^5$), *with estimated standard deviations in parentheses*

	x	y	z
Hf	27193 (2)	26207 (2)	24181 (2)
O(1*A*1)	17821 (38)	13168 (38)	18778 (41)
C(1*A*1)	15911 (59)	−1595 (57)	7321 (65)
C(2*A*1)	13603 (72)	−3779 (74)	−3080 (80)
C(3*A*1)	8814 (87)	−12774 (92)	−5979 (96)
C(4*A*1)	6479 (98)	−19081 (87)	1413 (114)
C(5*A*1)	8822 (86)	−16777 (74)	11906 (102)
C(6*A*1)	13596 (68)	−7784 (65)	14907 (78)
C(7*A*1)	20779 (57)	7800 (56)	10865 (62)
O(2*A*2)	31518 (38)	20026 (37)	9618 (41)
C(1*A*2)	33335 (59)	6159 (60)	−2550 (60)
C(2*A*2)	34118 (65)	12240 (69)	−10740 (69)
C(3*A*2)	39270 (74)	8108 (84)	−19243 (75)
C(4*A*2)	43589 (71)	−1966 (81)	−19251 (74)
C(5*A*2)	42791 (77)	−7889 (77)	−11026 (81)
C(6*A*2)	37660 (72)	−3866 (65)	−2496 (74)
N(7*A*2)	28305 (50)	10777 (47)	6091 (52)
O(1*B*1)	31717 (38)	39024 (38)	15372 (41)
C(1*B*1)	42480 (59)	52152 (56)	14477 (59)
C(2*B*1)	34448 (65)	59311 (62)	11453 (69)
C(3*B*1)	36379 (77)	68308 (69)	7222 (83)
C(4*B*1)	46315 (77)	70166 (68)	5894 (83)
C(5*B*1)	54255 (74)	62945 (71)	8649 (81)
C(6*B*1)	52355 (65)	53903 (65)	13002 (71)
C(7*B*1)	39750 (56)	42760 (53)	18674 (59)
O(2*B*2)	42052 (38)	29224 (38)	29268 (44)
C(1*B*2)	54594 (60)	40709 (66)	31308 (65)
C(2*B*2)	54466 (77)	49479 (80)	37687 (80)
C(3*B*2)	63705 (108)	52070 (111)	42462 (93)
C(4*B*2)	72578 (101)	45695 (139)	40738 (109)
C(5*B*2)	72460 (81)	36874 (120)	34618 (106)
C(6*B*2)	63248 (68)	33938 (84)	29619 (81)
N(7*B*2)	45298 (47)	38037 (47)	26126 (54)
O(1*C*1)	35263 (38)	11317 (35)	29426 (41)
C(1*C*1)	36463 (54)	−2555 (56)	40495 (62)
C(2*C*1)	38309 (62)	−10030 (60)	32677 (68)
C(3*C*1)	42574 (78)	−19826 (68)	35218 (81)
C(4*C*1)	45076 (72)	−21985 (71)	45458 (80)
C(5*C*1)	43356 (71)	−14399 (68)	53266 (75)
C(6*C*1)	38949 (63)	−4634 (62)	50887 (65)
C(7*C*1)	32288 (53)	7814 (56)	37395 (57)
O(2*C*2)	22460 (41)	23100 (37)	38771 (41)
C(1*C*2)	20614 (60)	11703 (65)	51621 (62)
C(2*C*2)	15187 (74)	3238 (78)	51829 (86)
C(3*C*2)	10733 (90)	1701 (102)	60799 (105)
C(4*C*2)	11208 (95)	8745 (130)	69011 (104)
C(5*C*2)	16350 (98)	17427 (115)	68813 (87)
C(6*C*2)	21301 (72)	18949 (81)	59697 (72)
N(7*C*2)	25203 (47)	13528 (46)	42448 (50)
O(1*D*1)	23447 (38)	41238 (38)	33129 (41)
C(1*D*1)	12349 (62)	56567 (59)	35294 (62)
C(2*D*1)	3234 (69)	57889 (71)	40090 (71)
C(3*D*1)	967 (86)	67144 (92)	45902 (87)
C(4*D*1)	7620 (105)	74791 (86)	46411 (102)
C(5*D*1)	16462 (98)	73321 (77)	41451 (93)
C(6*D*1)	19141 (74)	63985 (65)	35996 (80)
C(7*D*1)	15426 (57)	46430 (56)	30072 (59)
O(2*D*2)	12625 (38)	32585 (35)	19005 (41)
C(1*D*2)	443 (56)	46955 (57)	17563 (59)
C(2*D*2)	173 (65)	56260 (66)	13134 (74)
C(3*D*2)	−8763 (71)	60263 (75)	7946 (77)
C(4*D*2)	−17066 (68)	54726 (83)	7076 (80)
C(5*D*2)	−16653 (71)	45420 (90)	11504 (90)
C(6*D*2)	−7793 (62)	41396 (71)	16987 (75)
N(7*D*2)	9645 (47)	42482 (46)	22500 (50)

Results and discussion

Fig. 1 gives the bond parameters calculated from atomic coordinates. The estimated standard deviations are ~0·010 Å for bond distances within both the phenyl groups and the OCNO skeletons, ~0·005 Å for Hf—O bond lengths and ~0·01° for bond angles. In the following, the four NBPHA ligands are labelled *A*, *B*, *C*, *D*. Within each ligand, the phenyl groups attached to the CO and NO groups respectively are differentiated by numerical indices (*e.g.* *A*1, *A*2). C atoms of the aromatic rings are denoted C(1*A*1), C(2*A*1),..., C(6*D*2). In the same way, atoms of the OCNO skeletons are labelled O(1*A*1), C(7*A*1), N(7*A*2), O(2*A*2), and so on.

Fig. 2 is a perspective drawing of the Hf(NBPHA)$_4$ molecule.

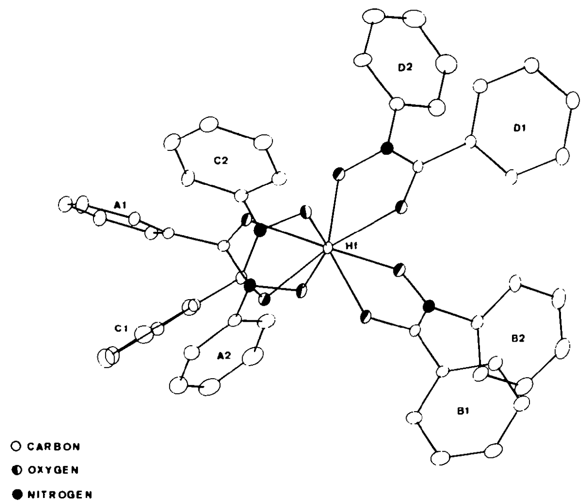

Fig. 2. Perspective drawing of the Hf(NBPHA)$_4$ molecule.

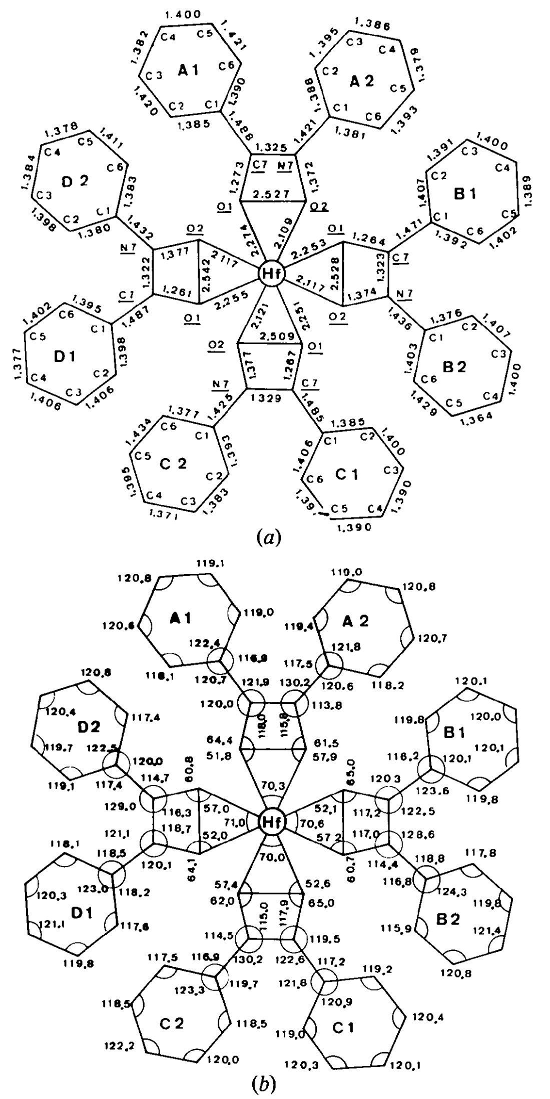

Fig. 1. (*a*) Interatomic distances (Å) and (*b*) bond angles (°).

Coordination polyhedron

The configuration of the HfO$_8$ group in Hf(NBPHA)$_4$ is shown in Fig. 3. As suggested by Lippard & Russ (1968), the coordination polyhedron for an eight-coordinate molecule can be identified by first calculating the angle of intersection between the two trapezoidal best planes of a supposed dodecahedron, and then by comparing the result so obtained with the values expected for the idealized dodecahedron (90°) and for the idealized square antiprism (77·4°). In fact, O atoms of the HfO$_8$ group can be considered as located at the corners of two interlocking distorted trapezoids, O(1*A*1)O(2*D*2)O(2*B*2)-O(1*C*1) and O(1*B*1)O(2*A*2)O(2*C*2)O(1*D*1). The corresponding mean trapezoidal planes, *T*1 and *T*2, are determined by the equations given in Table 4. The value

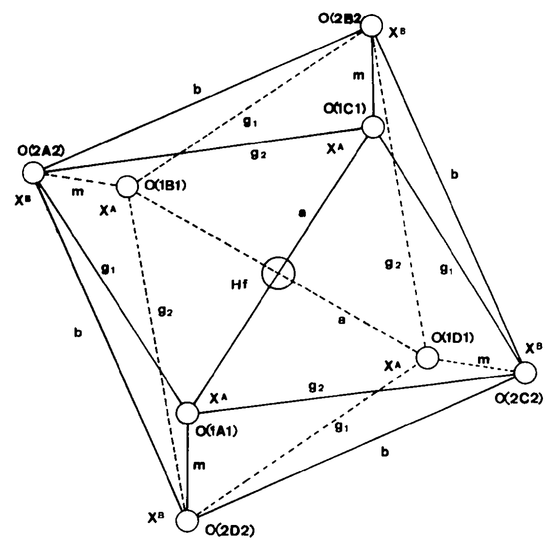

Fig. 3. The HfO$_8$ dodecahedron viewed along the quasi $\bar{4}$ axis.

for the dihedral angle between these two planes is 89·6°, and thus it may be concluded that the coordination polyhedron is unmistakably a dodecahedron.

As indicated by the data listed in Table 4, the distortion from planarity in the two trapezoidal figures is significant. The O atoms lie at distances ranging from 0·08 to 0·20 Å on both sides of the $T1$ and $T2$ mean planes, in such a way that the trapezoidal groups are twisted at the Hf site. A quite similar situation has been observed by Glen, Silverton & Hoard (1963) in $Na_4Zr(C_2O_4)_4.3H_2O$. It must be noted that atoms O(1*A*1), O(2*D*2), O(2*B*2) and O(1*C*1) are 0·13–0·20 Å from the mean plane $T1$, while atoms O(1*B*1), O(2*A*2), O(2*C*2) and O(1*D*1) are only 0·08–0·12 Å from the mean plane $T2$. This means that the amplitudes of rotational twisting are significantly different for the two trapezoidal groups. This difference is clearly indicated in Fig. 4, which is a view of the inner coordination group along the line of intersection of the mean trapezoidal planes. As a consequence of the observed deformations, all the symmetry elements of the regular dodecahedron are lost. However, the line of intersection of the mean trapezoidal planes can be considered as a quasi $\bar{4}$ axis.

The eighteen edges of a regular MX_8 dodecahedron are distributed among four classes, conventionally labelled a, b, m and g (Hoard & Silverton, 1963). On the other hand, full $\bar{4}2m$ symmetry requires two non-equivalent classes of ligands, X^A and X^B (see Fig. 3), and allows unequal bond lengths M–X^A and M–X^B. The values of the edge lengths in $Hf(NBPHA)_4$, as obtained by a calculation of O–O distances, are listed in Table 5. The g edges are here characteristically divided into two classes, g_1 and g_2, specified by quite

Table 4. *Equations of trapezoidal mean planes, with deviations (x,y,z are fractional coordinates)*

Plane $T1$: O(1*A*1)–O(2*B*2)–O(1*C*1)–O(2*D*2)

$$-5{\cdot}13x + 0{\cdot}21y + 12{\cdot}26z = 1{\cdot}618$$

O(1*A*1)	−0·203 Å	O(2*D*2)	0·131 Å
O(2*B*2)	−0·129	Hf	0·004
O(1*C*1)	0·202		

Plane $T2$: O(2*A*2)–O(1*B*1)–O(2*C*2)–O(1*D*1)

$$12{\cdot}16x - 0{\cdot}40y + 4{\cdot}35z = 4{\cdot}248$$

O(2*A*2)	−0·078 Å	O(1*D*1)	−0·121 Å
O(1*B*1)	0·121	Hf	0·006
O(2*C*2)	0·078		

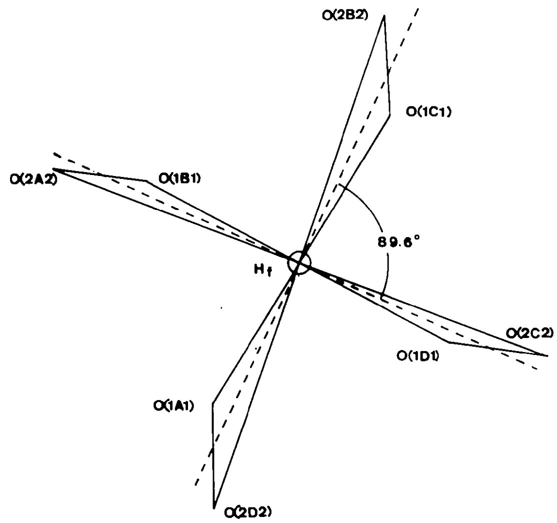

Fig. 4. View along the quasi $\bar{4}$ axis of the twisted trapezoidal planes.

Table 5. O–O *bond distances* (Å)

	Edge a	Edge m	Edge b	Edge g_2	Edge g_1
O(1*A*1)–O(1*C*1)	2·621 (7)				
O(1*B*1)–O(1*D*1)	2·619 (8)				
O(1*A*1)–O(2*D*2)		2·569 (7)			
O(1*B*1)–O(2*A*2)		2·561 (7)			
O(1*C*1)–O(2*B*2)		2·611 (7)			
O(1*D*1)–O(2*C*2)		2·556 (7)			
O(2*A*2)–O(2*B*2)			3·071 (8)		
O(2*B*2)–O(2*C*2)			3·174 (8)		
O(2*C*2)–O(2*D*2)			3·078 (7)		
O(2*D*2)–O(2*A*2)			3·144 (7)		
O(1*A*1)–O(2*C*2)				2·892 (7)	
O(1*B*1)–O(2*D*2)				2·852 (8)	
O(1*C*1)–O(2*A*2)				2·876 (8)	
O(1*D*1)–O(2*B*2)				2·857 (7)	
O(1*A*1)–O(2*A*2)					2·527 (8)
O(1*B*1)–O(2*B*2)					2·528 (7)
O(1*C*1)–O(2*C*2)					2·509 (7)
O(1*D*1)–O(2*D*2)					2·542 (7)
Average	2·620 (10)	2·374 (14)	3·117 (15)	2·869 (15)	2·527 (15)

different average lengths (2·53 ± 0·015 and 2·87 ± 0·015 Å respectively). When referring to Fig. 3, this clearly appears as a result of the twisting of the two trapezoidal groups. Moreover, the existence of two types of nonequivalent g edges requires the previously mentioned disappearance of both twofold axes and m symmetry planes in the HfO_8 polyhedron.

Two kinds of Hf—O bonds, corresponding to either X^A-type or X^B-type O atoms, are unambiguously distinguished within the inner coordination group. The respective average bond distances are Hf—O^A = 2·25 ± 0·01 Å and Hf—O^B = 2·12 ± 0·01 Å (see Table 6), and the ratio Hf—O^A/Hf—O^B is then 1·07 ± 0·01. This value is considerably higher than those observed in all other HfO_8 or ZrO_8 dodecahedra previously studied (Tranqui, Boyer, Laugier & Vulliet, 1977) and must be considered as one of the most striking features of this structure.

The shape parameters for an HfO_8 or ZrO_8 dodecahedron of $\bar{4}2m$ symmetry, as predicted by minimization of ligand–ligand repulsive energy (Hoard & Silverton, 1963; Kepert, 1965), are: average M—O = 2·19 ± 0·05 Å, M—O^A/M—O^B = 1·03, $a = m = 2{\cdot}57$ Å, $g = 2{\cdot}73$ Å, $b = 3{\cdot}28$ Å, $\theta^A = 35{\cdot}2°$, $\theta^B = 73{\cdot}5°$. The average M—O (M = Hf or Zr) distance is the mean value calculated from four accurate determinations in dodecahedral Hf^{IV} or Zr^{IV} compounds. θ^A and θ^B are the respective angles made by M—O^A and M—O^B bonds with the $\bar{4}$ axis. The average values of the shape parameters for the HfO_8 group in Hf(NBPHA)$_4$ are: Hf—O = 2·187 ± 0·005 Å, M—O^A/M—O^B = 1·07, a = 2·620 ± 0·005 Å, m = 2·574 ± 0·005 Å, g = 2·719 ± 0·005 Å, b = 3·117 ± 0·005 Å, θ^A = 35·5 ± 0·1°, θ^B = 73·05 ± 0·10°. A comparison of these data with those expected leads to the interesting conclusion that, as in all other dodecahedral chelates involving the HfO_8 or ZrO_8 group, the average inner coordination polyhedron is very close to a regular dodecahedron. In the more strongly deformed chelates, $Na_4Zr(C_2O_4)_4.3H_2O$ and Hf(NBPHA)$_4$, the distortion from the idealized dodecahedral configuration is primarily constituted by the rotational twisting of the two structurally independent trapezoidal groups. According to Glen *et al.* (1963), such a distortion would require little energy and then could be more easily achieved than other possible deformations of the regular dodecahedron. One then has good reason to expect the rotational twisting of the trapezoidal groups to take place in all strongly distorted dodecahedral systems, in such a way that the average geometry retains quasi $\bar{4}2m$ symmetry.

Table 6. Hf—O *bond lengths* (Å)

M–X^A bonds		M–X^B bonds	
Hf—O(1*A*1)	2·274 (5)	Hf—O(2*A*2)	2·108 (5)
Hf—O(1*B*1)	2·253 (5)	Hf—O(2*B*2)	2·117 (5)
Hf—O(1*C*1)	2·251 (5)	Hf—O(2*C*2)	2·121 (6)
Hf—O(1*D*1)	2·255 (5)	Hf—O(2*D*2)	2·117 (5)
Average	2·258 (10)		2·116 (10)

Ligands

The four bidentate NBPHA ligands are branched on the four g_1 edges of the HfO_8 dodecahedron, in such a way that O atoms of CO and NO groups occupy coordination sites of types X^A and X^B respectively. The arrangement of the ligands corresponds to the dodecahedral stereoisomer specified as II_d-*gggg* in the classification introduced by Hoard & Silverton (1963) for eight-coordinate $M(L)_4$ complexes.

The mean planes corresponding to the four OCNO skeletons and to the eight phenyl groups are determined by the equations given in Table 7. The maximum deviations of atoms from the mean planes are ~0·5 Å within the OCNO skeletons and ~0·02 Å within the aromatic rings. As indicated in Table 7, the two aromatic C atoms C(1) of each ligand [*e.g.* C(1*A*1) and C(1*A*2)] also belong to the chelating mean plane. On the other hand, the Hf atom lies substantially outside the OCNO planes, at distances ranging from 0·20 to 0·35 Å.

The bond parameters of the chelating rings are remarkably constant. The average N—O bond distance is 1·37 ± 0·02 Å. This value is close to that expected for a single N—O bond (1·42 Å). On the other hand, the mean values of the C—O and C—N bond lengths (1·27 ±0·02 and 1·32 ± 0·02 Å respectively) account

Table 7. *Equations of mean planes corresponding to phenyl groups and* OCNO *skeletons* (*x,y,z are fractional coordinates*)

Plane	
*A*1: C(1*A*1), . . . , C(6*A*1)	$11{\cdot}34x - 5{\cdot}66y - 1{\cdot}26z = 1{\cdot}798$
*A*2: C(1*A*2), . . . , C(6*A*2)	$11{\cdot}43x + 4{\cdot}88y + 4{\cdot}62z = 3{\cdot}999$
*B*1: C(1*B*1), . . . , C(6*B*1)	$0{\cdot}65x + 5{\cdot}34y + 11{\cdot}50z = 4{\cdot}715$
*B*2: C(1*B*2), . . . , C(6*B*2)	$-3{\cdot}54x - 7{\cdot}64y + 10{\cdot}86z = -1{\cdot}624$
*C*1: C(1*C*1), . . . , C(6*C*1)	$12{\cdot}75x + 5{\cdot}13y - 2{\cdot}03z = 3{\cdot}698$
*C*2: C(1*C*2), . . . , C(6*C*2)	$10{\cdot}14x - 6{\cdot}00y + 4{\cdot}39z = 3{\cdot}642$
*D*1: C(1*D*1), . . . , C(6*D*1)	$-4{\cdot}32x + 5{\cdot}04y + 10{\cdot}98z = 4{\cdot}270$
*D*2: C(1*D*2), . . . , C(6*D*2)	$4{\cdot}91x - 5{\cdot}18y + 10{\cdot}62z = 1{\cdot}431$
Ω*A*: O(1*A*1)–C(7*A*1)–C(1*A*1)–C(1*A*2)–N(7*A*2)–O(2*A*2)	$7{\cdot}66x - 6{\cdot}40y + 7{\cdot}72z = 1{\cdot}928$
Ω*B*: O(1*B*1)–C(7*B*1)–C(1*B*1)–C(1*B*2)–B(7*B*2)–O(2*B*2)	$-6{\cdot}78x + 6{\cdot}00y + 9{\cdot}06z = 1{\cdot}569$
Ω*C*: O(1*C*1)–C(7*C*1)–C(1*C*1)–C(1*C*2)–N(7*C*2)–O(2*C*2)	$9{\cdot}82x + 5{\cdot}83y + 6{\cdot}43z = 6{\cdot}024$
Ω*D*: O(1*D*1)–C(7*D*1)–C(1*D*1)–C(1*D*2)–N(7*D*2)–O(2*D*2)	$-8{\cdot}08x - 6{\cdot}57y + 9{\cdot}50z = -1{\cdot}417$

for a high degree of double-bond character. Because of the essentially single-bond character of C(7-)—C(1-) and N(7-)—C(1-) bonds, the internal hindrance for the rotation of phenyl groups about C—C and C—N bonds is expected to be small. The relative orientation of the aromatic rings then results from the minimization of the repulsive energy both within the molecule and between the molecule and its nearest neighbours. The angles between the various mean planes were calculated and are listed in Table 8. The structure of the Sn^{IV} compound $Cl_2Sn(NBPHA)_2$ has recently been determined (Harrison, King & Richards, 1976). Although this complex has quite a different coordination number and spatial configuration, the bond parameters of the NBPHA ligands are in very close agreement with those measured in the present work.

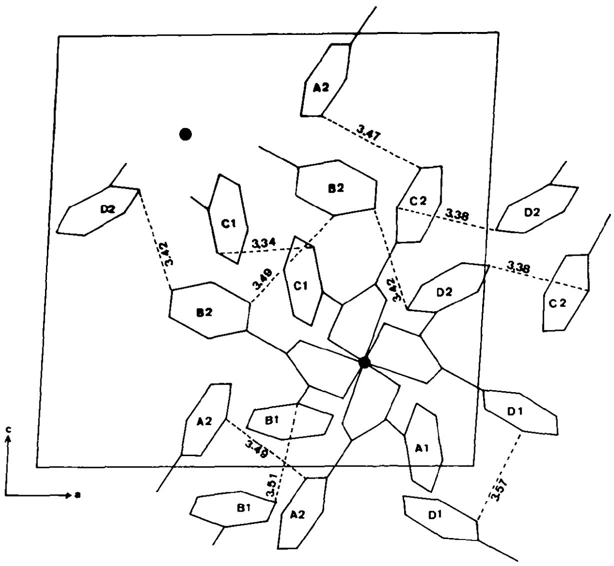

Fig. 5. Projection onto the *ac* plane of the $Hf(NBPHA)_4$ molecule and of the nearest-neighbour phenyl groups.

Fig. 5 shows an $Hf(NBPHA)_4$ molecule and its immediate environment as viewed along the *b* axis. Only the phenyl groups of the adjacent molecules are represented in this picture, for the complexity of the system does not allow the complete packing diagram to be clearly shown. The shortest intermolecular distances are ~3·34 Å and correspond to normal van der Waals contacts between aromatic rings. The close interpenetration of adjacent molecules, as displayed in Fig. 5, appears as evidence of the significant role played by intermolecular ligand–ligand repulsions in the determination of both the molecular structure and the packing arrangement in the crystal.

The preceding data allow an interpretation of the structure of $Hf(NBPHA)_4$ in terms of ligand–ligand interactions and metal–ligand π bonding. As suggested by Bonds *et al.* (1971), the stereochemistry of dodecahedral transition-metal chelates can be explained on the assumption that (1) the bite and steric requirements of the bidentate ligand determine which edges of the coordination polyhedron are to be spanned, and (2) the nature of the metal–ligand bond determines the distribution of the donor atoms among the coordination sites (Orgel's rule). The recently solved structures of tetrakis(*N*-ethylsalicylideneiminato)zirconium(IV) (Bradley *et al.*, 1970) and tetrakis(8-quinolinato)zirconium(IV) (Lewis & Fay, 1974) fit these assumptions. In these two $M(AB)_4$ complexes, the large bite of the chelating agent (2·749 and 2·78 Å respectively) allows the ligands to span the four *g* edges of a II_d-*gggg* dodecahedral stereoisomer. This spatial configuration is also energetically favoured by ligand–ligand repulsions. On the other hand, the occupancy of the coordination sites X^A and X^B is in full agreement with Orgel's rule for d^0 complexes: the π-donor phenolic O atoms are located at X^B sites adjacent to the vacant d_{x2-y2} π orbital of the metal, while the X^A sites are occupied by the poor π-donor N atoms.

In view of the smallness of the bite of the NBPHA ligand, a I_d-*mmmm* configuration would be anticipated for $Hf(NBPHA)_4$. Then it may be concluded that (1)

Table 8. *Angles* (°) *between mean planes*

Planes	*A*1	*A*2	*B*1	*B*2	*C*1	*C*2	*D*1	*D*2	*ΩA*	*ΩB*	*ΩC*
*A*1	0										
*A*2	56·7	0									
*B*1	76·6	56·5	0								
*B*2	89·1	87·6	61·2	0							
*C*1	48·6	29·8	84·3	61·9	0						
*C*2	25·3	49·2	81·4	67·3	57·3	0					
*D*1	56·5	77·9	21·8	58·7	75·7	80·5	0				
*D*2	60·9	56·8	53·7	37·6	80·5	35·6	66·8	0			
ΩA	42·6	53·3	69·0	50·7	70·0	17·6	84·5	18·4	0		
ΩB	41·7	89·4	35·4	66·9	67·4	65·7	14·8	80·9	81·1	0	
ΩC	66·9	11·5	45·4	87·2	39·9	55·6	66·4	54·7	55·7	77·8	0
ΩD	70·9	69·3	66·4	21·9	41·2	88·9	54·9	59·0	72·7	57·2	76·9

the actual arrangement of the ligands is primarily determined by ligand repulsions, and (2) the excess of repulsive energy within a I_d-*mmmm* configuration would be prohibitive in comparison with the energy involved in the deformation of the observed II_d-*gggg* stereoisomer. This deformation clearly results from the constraints imposed by the rigidity and small bite of the chelating ring.

On the other hand, the branching of the ligand on a g edge of the dodecahedron is achieved through two chemically different O atoms. Owing to the single-bond character of the N—O bonds, the contribution of $p_\perp$ orbitals of the NO-group O atoms to the π stabilization of the OCNO rings is negligible. The π-donor capability of the NO groups is then undoubtedly higher than that of the CO groups. According to Orgel's rule for d^0 complexes, O atoms of the NO groups are expected to be located at the X^B coordination sites. This prediction is confirmed by the determination of the structure, and the Hf(NBPHA)$_4$ chelate then appears as an example of an $M(AA')_4$ dodecahedral system whose stereochemistry can be rationalized with Orgel's rule. The $p_\perp$ orbitals of the X^B-type O atoms are expected to contribute significantly to Hf—O^B bonds through π-bonding interactions with the empty d_{x2-y2} orbital of $\mathrm{Hf}^{\mathrm{IV}}$. These interactions could account for both the shortening of the Hf—O^B bonds and the unusually high bond-length ratio Hf—O^A/Hf—O^B observed in this complex.

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