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Hyperfine Quadrupole Coupling and π Bonding in Dodecahedral Chelates of Hafnium(IV)

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Time-differential-perturbed angular correlation experiments using the 133–482-keV γ–γ cascade of the ^{181}Ta nucleus have been performed in order to determine the hyperfine quadrupole couplings in various d^0 dodecahedral chelates of hafnium(IV). The hyperfine data are analyzed within the frame of both the point-charge model considering the actual geometry of the coordination polyhedra and the valence bond picture. Our analysis indicates a significant contribution of π bonding to the stabilization of these systems. The charge transferred onto the metal via $\pi \rightarrow d_{x^2-y^2}$ interactions is estimated at about 20% of the overall charge donated by the ligands in the tetrakis(*N*-benzoyl-*N*-phenylhydroxylaminato)hafnium(IV) and 16% in the tetrakis(*N*-nitroso-*N*-phenylhydroxylaminato)hafnium(IV). The overall charge donated by the ligands onto the valence orbitals of the metal stands between -0.7 and $-1.2e$, which attests the important ionic character of the hafnium–oxygen bonds in these eight-coordinate chelates.

Introduction

The decisive role played by d–π interactions in determining the stereochemistry of eight-coordinate dodecahedral complexes of transition elements was first suggested by Orgel.[1] Initially developed for complexes of d^1 or d^2 metal ions, Orgel's ideas have been later on extended to d^0 complexes and may be summarized as follows: in dodecahedral complexes of the type MA_4B_4, the distribution of the two different ligands onto the two nonequivalent coordination sites A and B[2] should depend on both the electronic configuration of the metal ion and the relative π-bonding capabilities of the ligands. For d^0 complexes, the better π-donor ligands (or ligating atoms for polydentate ligands) should occupy the B positions on the dodecahedron. The inverted situation would be expected in complexes of d^1 or d^2 metal ions. Such predictions are based on the following ligand-field argument: in dodecahedral complexes of D_{2d} (or lower) symmetry, the b_1 ($d_{x^2-y^2}$) level is more stable than any other and is capable of forming strong π bonds with the ligands placed on the B coordination sites. However, as pointed out by Archer, Bonds, and Hamilton,[3] a full picture of π bonding in dodecahedral complexes of transition metals must include all the d orbitals of the central atom. Thus, according to the results of angular overlap calculations, both the A and B ligands would be substantially involved in π-bonding interactions.[3] From the experimental point of view, several structures obeying completely[3-6] or only partially[7] Orgel's rules have been reported, but the number of MA_4B_4 complexes whose structures are known is still too small for valid conclusions to be reached about the importance and the nature of π bonding in these molecular species.

The determination of the electric field gradient (efg) at the nucleus of the central atom can provide a new insight into metal–ligand bonds in dodecahedral complexes. Effectively, the efg tensor is directly related to the charge distribution around the nuclear probe. Measurements of electric field gradients in dodecahedral d^0 complexes are of particular interest for (i) the charge distribution around the metal is expected to be significantly influenced by any eventual charge transfer from the ligands onto the $d_{x^2-y^2}$ orbital of the metal via specific d–π interactions and (ii) this influence would result in specific modifications of the efg tensor which could be reasonably interpreted by using a simple efg model such as the donated-charge model.[8] Moreover, such experiments can provide valuable information concerning the importance of π-bonding effects in complexes involving identical monodentate or symmetrical bidentate ligands to which Orgel's rule does not apply.

For eight-coordinate d^0 complexes of the group 4B transition metals, the study of the angular correlations of the γ rays emitted from the radioactive ^{44}Ti and ^{181}Hf isotopes is the only way available for determining accurately both the magnitude and the asymmetry of the electric field gradient at the site of the central nucleus. When the quadrupole moment of the intermediate level in a γ_1–γ_2 nuclear cascade couples with an electric field gradient, one observes a perturbation in the anisotropic angular distribution of the intensity of the second radiation (γ_2) with respect to the direction at which the first radiation (γ_1) is detected. In order to obtain the values of the quadrupole-coupling parameters, we determined the time evolution of this perturbation during the lifetime of the intermediate nuclear state by performing time-differential-perturbed angular correlation (TDPAC) experiments. Typically, when ^{181}Hf is used as nuclear probe, this technique allows one to measure quadrupole frequencies ω_Q within the range 20–200 $\mathrm{Mrd{\cdot}s^{-1}}$ with an accuracy of about 1%. TDPAC measurements of electric field gradients in several chelates[9-13] and organometallic compounds[14] of hafnium(IV) have been already reported. Recently, Vulliet, Baudry, Boyer, and Tissier[11] have been able to give a coherent interpretation of the quadru-

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pole-coupling parameters measured in the two chelates sodium tetrakis(oxalato)hafniate(IV) trihydrate and potassium tetrakis(oxalato)hafniate(IV) pentahydrate by entering the real atomic positions within the HfO_8 coordination groups into a point-charge efg model. Their conclusion is that the hyperfine-quadrupole data are consistent with the existence of significant interactions between the hafnium $d_{x^2-y^2}$ orbital and the π orbitals of the symmetrical oxalate ligand.

The purpose of the present work is to use the same model in order to interpret the electric field gradients determined by TDPAC experiments in various neutral dodecahedral chelates of hafnium(IV).

Experimental Section

Sample Preparations. $Hf(BPHA)_4$. Tetrakis(*N*-benzoyl-*N*-phenylhydroxylaminato)hafnium(IV) [$Hf(BPHA)_4$] has been prepared according to the method described by Ryan.[15] In order to obtain well-crystallized samples, we dissolved the fine powder so obtained in methylene chloride up to 150 g·L^{-1}. Acetone was then added in a ratio of 5/1, and the solution was evaporated at room temperature for 1 or 2 weeks. In this way, we have been able to produce single crystals, and the structure of $Hf(BPHA)_4$ has been recently reported.[6]

Hf(cupferrate)$_4$. Tetrakis(*N*-nitroso-*N*-phenylhydroxylaminato)hafnium(IV) [Hf(cupferrate)$_4$] was prepared according to the procedure described by Karlysheva and Sheka.[16] The material was recrystallized by using the same method as for $Hf(BPHA)_4$. The structure of the isomorphous zirconium compound has been solved by Mark.[17]

$Hf(T)_4$ and $Hf(T)_4$·DMF. Tetrakis(tropolonato)hafnium(IV) [$Hf(T)_4$] was prepared by mixing a solution of $HfOCl_2$ in a 50% water–methanol mixture with a solution of tropolone in 50% water–methanol, as indicated by Hutchinson, Eversdyk, and Olbricht.[18] The solution was refluxed for 1 h and then filtered, and the product was finally dried under vacuum at room temperature. At this stage, as shown by accurate thermogravimetric analysis, the tetrakis(tropolonato)hafnium(IV) was monohydrated.[19] Anhydrous $Hf(T)_4$ was obtained by vacuum pumping or by heating at 50 °C. The anhydrous chelate has been found to be rather hygroscopic and should be kept in a vacuum-sealed container.

The ability of $Hf(T)_4$ in forming molecular complexes of stoichiometry 1:1 with various organic molecules was first recognized by Boyer, Tissier, and Vargas.[20] Molecular complexes of $Hf(T)_4$ with chloroform, methylene chloride, and dimethylformamide [$Hf(T)_4$·DMF] are obtained by dissolving $Hf(T)_4$ in the organic solvent at high temperature and by evaporating the solvent. Crystals of $Hf(T)_4$·DMF could be produced by this method, and the structure of this molecular complex has been solved.[21]

Hf(8-quin)$_4$. According to the procedure reported by Vinogradov and Shpinel,[22] tetrakis(8-hydroxyquinolinato)hafnium(IV) [Hf(8-quin)$_4$] was obtained by mixing oxalic acid and 8-hydroxyquinoline with a solution of hafnium oxychloride in 10% HCl. The solution was heated up to 80 °C, and the chelate was then precipitated at pH 7 by adding a dilute aqueous solution of ammonia. No attempt was made to recrystallize the fine yellow powder so obtained. Structural data recorded by Lewis and Fay[5] from a single crystal of isomorphous Zr(8-quin)$_4$ containing three toluene molecules per unit cell support a dodecahedral D_2 *gggg* stereochemistry for this chelate.

The unstable ^{181}Hf isotope ($T_{1/2}$ = 44 days) is produced by thermal neutron capture from ^{180}Hf whose isotopic abundance is about 35%. ^{181}Hf-labeled samples used in our TDPAC experiments were then prepared from hafnium oxychloride previously irradiated in a thermal neutron flux of 10^{14} n·cm^{-2}·s^{-1} for 4 h.

TDPAC Experiments. A γ–γ-perturbed angular correlation experiment requires an experimental setup which is capable of recording the number of events corresponding to the emission of two successive γ rays, γ_1 and γ_2, by the same nucleus. These events are recorded as a function of the time interval t between the emission of γ_1 and γ_2, for different values of the angle θ between the directions of emission of the two radiations.

In our hyperfine-quadrupole-coupling measurements, the probe was the 482-keV level of the ^{181}Ta nucleus. This $I = {}^5/_2$ level has a quadrupole moment $Q = -2.5$ b and a mean life $\tau_N = 15.8 \times 10^{-9}$ s. TDPAC experiments were performed on the γ_1(133 keV)–γ_2(482 keV) cascade fed by β^- decay from ^{181}Hf by using three-detector fast–slow coincidence circuitry. The γ rays were detected by NaI(Tl) scintillators associated with Radiotechnique 56 DVP 03 photomultipliers and allowing a time resolution of about 2×10^{-9} s. The strong quadrupole coupling observed in Hf(8-quin)$_4$ has been measured by using a plastic scintillator for detecting the 133-keV radiation. The time resolution was then reduced to 1.3×10^{-9} s.

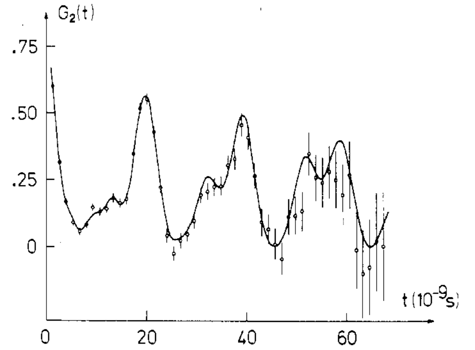

Figure 1. Room-temperature TDPAC spectrum of Hf(cupferrate)$_4$. The solid line results from a least-squares fit of experimental data with the $G_2^{\mathrm{th}}(t)$ function corrected for Lorentzian frequency distribution and time-resolution effects.

The theory of γ–γ TDPAC[23,24] shows that the hyperfine-coupling parameters are included in some function $G_2(t)$ which is expressed in terms of the measured coincidence counting rates $N(\theta,t)$ as

$$G_2(t) = \frac{10}{7A_2}\left[\frac{5N(\pi,t) + 4N(3\pi/4,t) - 9N(\pi/2,t)}{N(\pi,t) + 8N(3\pi/4,t) + 6N(\pi/2,t)}\right]$$

A_2 is a coefficient characteristic of the γ–γ nuclear cascade. In our experiments, its value, corrected for finite solid angles of the detectors,[25] was taken equal to −0.25.

On the other hand, for an $I = {}^5/_2$ intermediate nuclear state interacting with a randomly oriented electric field gradient, the theoretical expression of the $G_2(t)$ function is

$$G_2^{\mathrm{th}}(t) = S_{k0}(\eta) + \sum_{n=1}^{3} S_{kn}(\eta) \cos\,[f_n(\eta)\omega_Q t]$$

The quadrupole frequency ω_Q and the asymmetry parameter η are defined by the two relations

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar}, \quad \eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (\eta \in [0,1])$$

where V_{xx}, V_{yy}, and V_{zz} are the components of the efg tensor in its principal axes. It must be remembered here that the sign of V_{zz} cannot be determined from a TDPAC experiment. The $S_{k0}(\eta)$, $S_{kn}(\eta)$, and $f_n(\eta)$ coefficients are calculated from the eigenvalues and the eigenstates of the hyperfine-quadrupole Hamiltonian.

In order to extract the values of ω_Q and η, we fitted the theoretical $G_2^{\mathrm{th}}(t)$ functions corrected for time-resolution effects and for efg inhomogeneities giving rise to frequency distributions[26] to experimentally determined $G_2(t)$ values by using a weighted least-squares-fit procedure. Lorentzian frequency distributions characterized by their relative half-widths δ have been assumed in our calculations. As a typical example, the time-dependent patterns of experimental and theoretical $G_2(t)$ functions relative to Hf(cupferrate)$_4$ are presented in Figure 1.

Results

The values of the quadrupole-coupling parameters measured by TDPAC experiments in the various hafnium(IV) chelates considered here are listed in Table I.

An unusually steep variation of the quadrupole frequency with temperature has been observed in the complex $Hf(T)_4$·DMF. This variation was attributed to the existence of weakly hindered librational motions within dimethylformamide.[12] In order to minimize the influence of these motions, we preferred to take into account, in the particular case of $Hf(T)_4$·DMF, the quadrupole-coupling parameters obtained at low temperature (170 K). On the other hand, the values of ω_Q and η relative to $Hf(T)_4$ are quite different from those previously

Table I. Quadrupole-Coupling Parameters Determined by Room-Temperature TDPAC Experiments in Various Dodecahedral Eight-Coordinate Chelates of Hf(IV)

compd	$\lvert\omega_Q\rvert$, Mrd·s^{-1}	η	δ,[a] %	ref
Hf(8-quin)$_4$	170.0 ± 3	0.61 ± 0.03	6	this work
Hf(BPHA)$_4$	102.2 ± 0.5	0.38 ± 0.01	1	this work
Hf(cupferrate)$_4$	53.5 ± 0.5	0.25 ± 0.01	1	this work
Hf(T)$_4$	44.0 ± 0.2	0.60 ± 0.01	3	12
Hf(T)$_4$·DMF[b]	43.5 ± 0.5	0.37 ± 0.02	10	12

[a] Relative half-width of the Lorentzian frequency distribution used in our least-squares-fit calculations. [b] Quadrupole-coupling parameters measured at $T = 170$ K.

reported[9] for the same compound prepared according to the method proposed by Muetterties and Wright.[27] As suggested in a recent paper by Baudry, Boyer, and Tissier,[12] solid samples of good quality could not be obtained by this last procedure.

The presence of two ^{181}Ta sites with distinct quadrupole couplings in the TDPAC spectra relative to the complexes Hf(BPHA)$_4$ and Hf(cupferrate)$_4$ have been previously observed.[9] At that time, it was suggested that these two sites could be associated with two different isomeric configurations of the same chelate. However, a more precise examination of this question in a number of hafnium chelates shows that a more or less important "background" must be systematically assumed in order to fit the TDPAC spectra satisfactorily. This "background" appears as resulting from the interaction of some fraction of nuclei with an ill-defined and broadly distributed electric field gradient. The origin of this phenomenon remains somewhat unclear, but we feel that it might well be found in the "aftereffects" of the β^- decay of the ^{181}Hf nucleus.[11]

Discussion

As in the series of alkali metal tetrakis(oxalato)hafniates,[11] the values of the asymmetry parameters are widely distributed and significantly different from zero in all cases. Owing to the r^{-3} dependence of the electric field gradient, it is usually assumed that the quadrupole interaction arises essentially from the charges situated within the first coordination sphere of the probe nucleus. According to structural data, the two *mmmm* dodecahedral isomers Hf(cupferrate)$_4$ and Hf(T)$_4$ as well as the *gggg* isomer Hf(BPHA)$_4$ display coordination polyhedra with significant distortions from the D_{2d}-$\bar{4}2m$ geometry. If the deformations are ignored, the ideal configuration of each coordination group displays a fourfold symmetry which requires the asymmetry parameter of the electric field gradient to be zero. As axial efg tensors are not observed in these compounds, it clearly appears that the full interpretation of the quadrupole couplings requires a model which takes into account the actual geometry of the coordination polyhedra. This point has been already emphasized by La Rossa and Brown[28] in their study of cobaloximes by ^{59}Co nuclear quadrupole resonance experiments. The influence of geometrical deformations on the quadrupole-coupling parameters in dodecahedral systems has been recently examined by Vulliet et al.[11] Point-charge and/or valence-bond calculations show that these parameters are extremely sensitive to some basic deformations frequently observed in dodecahedral structures such as the lack of orthogonality between the two ABBA trapezoidal planes and the dispersion in metal–ligand distances. As expected, this sensitivity is especially sharp for the asymmetry parameter and to a smaller extent for the sign of the greatest principal component V_{zz} of the efg tensor. As a consequence of the fact that the real structures of the eight-coordinate systems under study display no symmetry element, the spd hybridization scheme for the valence orbitals of the metal cannot be achieved without ambiguity. The use of efg models based on the Townes and Dailey approach,[29] in which the electric field gradient at the central nucleus is predominantly determined by the populations of the valence atomic orbitals of the metal, is then in general unworkable for interpreting quadrupole couplings in such systems.

On the contrary, the point-charge picture of the donated-charge model, which has been successfully used in six-coordinate systems presenting significantly distorted geometries,[28,29] appears to be well suited to our problem. In order to apply this model to bidentate chelates, it is convenient to assume that each metal–ligand bond can be reduced to two independent bonds between the central atom (M) and the ligating atoms (L) of the polyatomic bidentate ligand. Then, the overall electric field gradient at the metal site is expressed as a sum of axially symmetric partial field gradients attached to the various M–L bonds. If [L] is the partial field gradient associated with a particular M–L bond, then the principal components of the efg tensor are given by the expressions

$$\begin{aligned} V_{xx} &= \sum_{L=1}^{8} [L]\tfrac{1}{2}(3 \sin^2 \theta_L \cos^2 \phi_L - 1) \\ V_{yy} &= \sum_{L=1}^{8} [L]\tfrac{1}{2}(3 \sin^2 \theta_L \sin^2 \phi_L - 1) \qquad (1) \\ V_{zz} &= \sum_{L=1}^{8} [L]\tfrac{1}{2}(3 \cos^2 \theta_L - 1) \end{aligned}$$

where θ_L and ϕ_L are the two angles which determine the direction of the bond with respect to the principal axes of the tensor. In the point-charge picture of this model, the populations of M–L bonds are represented by effective point charges Q_L attached to the ligating atom positions. Therefore

$$[L] = (1 - \gamma_\infty)(2Q_L/r_L^3) \qquad (2)$$

$$[L] = (1 - \gamma_\infty)\frac{2q_L}{r_L^3} + (1 - R)q_L'\langle 3 \cos^2 \theta - 1\rangle_L \langle r^{-3}\rangle_L \qquad (2')$$

r_L is the M–L distance and q_L the charge resident on the ligating atom. On the other hand, since we are dealing with complexes of a d^0 metal ion, the second term of expression 2′ represents the contribution due to the charge q_L' donated by the ligand L onto the valence-bond orbital of the metal. As usual, the two Sternheimer coefficients $(1 - R)$ and $(1 - \gamma_\infty)$ are introduced in order to take into account the polarization effects on the core orbitals of the central ion.[30]

According to the valence-bond picture and/or ligand-field arguments, the bonds between the metal and the atoms located respectively at the A and B vertices of the coordination polyhedron in a dodecahedral complex are expected to be nonequivalent. Then, assuming that the M–L bonds are divided into two groups of four equivalent bonds, the V_{zz} component of the overall efg tensor can be expressed as

$$V_{zz} = \tfrac{1}{2}\sum_i (3 \cos^2 \theta_i - 1)[A_i] + \tfrac{1}{2}\sum_j (3 \cos^2 \theta_j - 1)[B_j] \qquad (3)$$

In this expression $[A_i] = 2(1 - \gamma_\infty)Q_A/r_{A_i}^3$ and $[B_j] = 2(1 - \gamma_\infty)Q_B/r_{B_j}^3$ are the partial field gradients associated with M–A$_i$ and M–B$_j$ bonds, respectively. Similar expressions are easily obtained for the V_{xx} and V_{yy} components of the efg tensor. An important point to be noted here is that, unlike the quadrupole frequency which depends on both Q_A and Q_B, the asymmetry parameter is entirely determined by the effective charge ratio Q_B/Q_A. The behavior of the calculated quadrupole-coupling parameters with respect to the Q_B/Q_A ratio within the range $0.5 \le Q_B/Q_A \le 3$ and for $Q_A = -e$ is shown in Figures 2–4 for the three chelates Hf(BPHA)$_4$, Hf(cupferrate)$_4$, and Hf(T)$_4$·DMF, respectively. The efg tensor was obtained by entering the real coordinates of the oxygen atoms located on the vertices of the coordination polyhedra into the point-charge calculation. It was first calculated within a molecular frame-

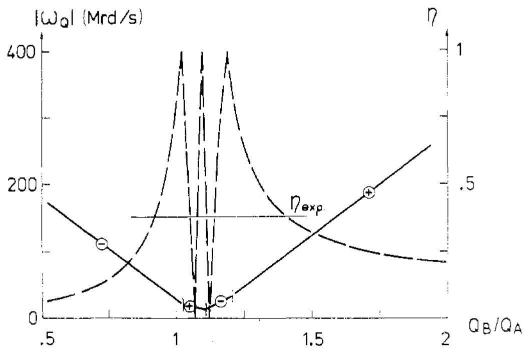

Figure 2. Plot of $|\omega_Q|$ (solid line) and η (broken line) vs. the effective charge ratio Q_B/Q_A in Hf(BPHA)$_4$. Vertical lines indicate sign changes of V_{zz} (this sign is shown within circles).

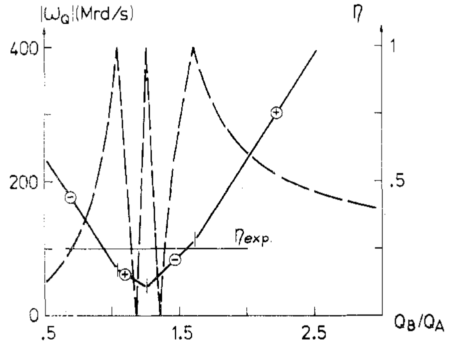

Figure 3. Plot of $|\omega_Q|$ (solid line) and η (broken line) vs. the Q_B/Q_A ratio in Hf(cupferrate)$_4$.

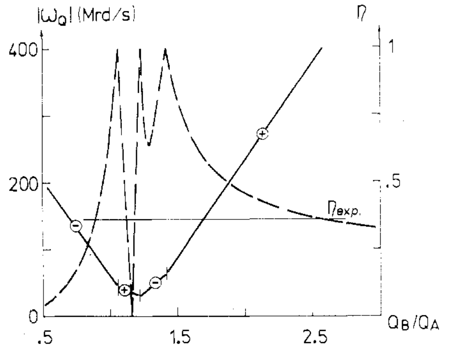

Figure 4. Plot of $|\omega_Q|$ (solid line) and η (broken line) vs. the Q_B/Q_A ratio in Hf(T)$_4$·DMF.

work and was then diagonalized in order to obtain both the principal components and the directions of the principal axes. The lack of data about the positions of ligating atoms in Hf(8-quin)$_4$ did not allow performing similar calculations for this chelate.

From a qualitative point of view, it must be noted that (i) the experimental values of the asymmetry parameters η are not found for $Q_B/Q_A = 1$ and (ii) the calculated asymmetry parameters display rapidly oscillating patterns. As a consequence, the asymmetry parameter measured in a particular system is found for several values of the Q_B/Q_A ratio. The effective charges Q_A and Q_B which reproduce the quadrupole-coupling parameters determined by TDPAC measurements in the three chelates under consideration are listed in Table II. The sign of the V_{zz} component of the efg tensor calculated for each pair of effective point charges (Q_A,Q_B) is also given in the same table. For the two complexes Hf(BPHA)$_4$ and Hf(cupferrate)$_4$, this sign has to be compared with the positive sign obtained by Mössbauer experiments performed at liquid-helium temperature on the $0^+ \rightarrow 2^+$ transition of the ^{178}Hf isotope.[31]

Table II. Effective Point Charges That Reproduce the Experimental Quadrupole Coupling Parameters in Three Dodecahedral Hf(IV) Chelates

				sign of V_{zz}		
compd	Q_B/Q_A	Q_A/e	Q_B/e	calcd	exptl[b]	$\Delta q/e$[c]
Hf(BPHA)$_4$	0.92	−2.0	−1.85	−	+	−1.9
	1.05	−5.5	−5.8	+		−6.9
	1.07	−6.8	−7.3	+		−8.7
	1.11	−6.8	−7.55	−		−8.9
	1.14	−5.0	−5.7	−		−6.5
	1.40[d]	−1.12[d]	−1.57[d]	+		−1.1[d]
Hf(cupferrate)$_4$	0.70	−0.30	−0.21	−	+	+0.3
	1.15[d]	−0.96[d]	−1.10[d]	+		−0.7[d]
	1.20[d]	−1.06[d]	−1.27[d]	+		−0.9[d]
	1.33	−0.96	−1.28	−		−0.8
	1.40	−0.77	−1.08	−		−0.6
Hf(T)$_4$·DMF	0.89	−0.46	−0.41	−		+0.1
	1.13[d]	−1.13[d]	−1.28[d]	+		−0.9[d]
	1.18[d]	−1.30	−1.53[d]	+		−1.2[d]
	2.60	−0.11	−0.28	+		+0.4

[a] Q_A and Q_B are located on the A and B vertices of the coordination polyhedron, respectively. [b] Determined at $T = 4$ K. [c] Overall charge transferred from the ligands onto the metal ion; calculated from eq 5. [d] Acceptable solutions in view of the sign of V_{zz} and the Δq values.

On the other hand, it is of interest to estimate the donated charge q_L' corresponding to an effective point charge Q_L. Such an estimation can be achieved as follows: q_0 being the net charge on a ligating atom before the complexation, then $q_L = q_0 - q_L'$, and from relations 2 and 2′ it can be deduced that

$$q_L' = \frac{Q_L - q_0}{\frac{1}{2}[(1 - R)/(1 - \gamma_\infty)]\langle 3\cos^2\theta - 1\rangle_L \langle r^{-3}\rangle_L r_L^3 - 1} \tag{4}$$

In this formula, the mean values of the operators $(3\cos^2\theta - 1)$ and r^{-3} have to be calculated by using valence-bond orbitals localized as far as possible in the region of the considered M–L bond. Thus, $\langle 3\cos^2\theta - 1\rangle_L \simeq 2$. On the other hand, an estimation of $\langle r^{-3}\rangle_L$ can be made by using an sp^{3}d^4 hybridization scheme for the valence orbitals of the metal ion. Relativistic calculations performed by Desclaux[32] for Ta^{2+}, Ta^{3+}, and Ta^{4+} free-ion configurations show that the weight-average quantity $\overline{\langle r^{-3}\rangle^{sp^3d^4}}$ is a smoothly varying function of the net charge on the central atom. For the Ta^{3+} configuration, the following values are obtained: $\langle r^{-3}\rangle_{5d} = 8.1$ au, $\langle r^{-3}\rangle_{6p} = 12$ au, $\overline{\langle r^{-3}\rangle^{sp^3d^4}} \equiv \langle r^{-3}\rangle_L = 7.5$ au. According to the more recent calculations of core polarization effects,[33,34] values of 0.15 and −64 are reasonably expected for R and γ_∞, respectively. Thus, with $r_L = 2.20$ Å, which corresponds to the average value of M–L distances measured in the three chelates under study, and $q_0 = -0.5$ e, eq 4 gives $q_L' \simeq (Q_L + 0.5\text{ e})/6$. The overall charge transferred from the ligands to the valence orbitals of the metal is then

$$\Delta q \simeq \tfrac{2}{3}(Q_A + Q_B + e) \tag{5}$$

The Δq values calculated from this expression are given in the last column of Table II. For the complexes under study, the total charge donated by the four ligands onto the atomic orbitals of the Ta^{5+} ion necessarily stands somewhere between 0 and −5*e*. On the basis of this physicochemical argument and by taking into account the sign of V_{zz} determined by Mössbauer spectroscopy, we easily see that only one of the six pairs of effective charges (Q_A,Q_B) that reproduce the electric field gradient measured in Hf(BPHA)$_4$ is acceptable. In the same way, there are two acceptable pairs (Q_A,Q_B) attached to the cupferrate and tropolonate ligands. The confidence which can be attributed to these results, and then to the conclusions reached later on, depends on the validity of eq 5 in order to estimate the charge transferred onto the metal ion. Actually, it is not easy to get an idea of the errors made on quantities such as the Sternheimer factors as well as the mean values $\langle r^{-3}\rangle_L$ and $\langle 3\cos^3\theta - 1\rangle_L$ which enter eq 4. The function $(3\cos^2\theta - 1)$ varies quite slowly in the range of small angles, and we believe the overestimation of the quantity $\langle 3\cos^2\theta - 1\rangle_L$ to be hardly exceeding 10%. On the other hand, due to the extension of metal orbitals in the complex, the mean value $\langle r^{-3}\rangle_L$ calculated from free-ion orbitals is expected to be slightly overestimated as well. The major source of uncertainty very probably arises from the evaluation of core polarization effects. For example, the free-ion $(1 - \gamma_\infty)$ values are usually found to be significantly smaller than experimental values measured for ions embedded in solids.[35] Beyond these uncertainties, an important point is that the same oversimplified calculations performed in sodium and potassium tetrakis(oxalato)hafniates lead to Δq values within the range $[-1.6e, -2.2e]$,[11] in good agreement with the conclusions reached by Johnson and Larsen[36] about the character of hafnium–oxygen bonds in the $Hf(C_2O_4)^{4-}$ anion. Hafnium–oxygen bonds would have the same character as aluminum–oxygen bonds in aluminum trioxalato anion which are 50% covalent according to the results given by Raman spectroscopy.[37] The realistic Δq values obtained for the $Hf(C_2O_4)^{4-}$ anion in two different compounds suggest that the overall donated charges calculated from expression 6 are probably not in error by more than 20%. Consequently, our conclusions would not be challenged by a more accurate estimation of the ligand → metal charge transference.

Returning to the results presented in Table II, we observe that the acceptable solutions correspond in all cases to Q_B/Q_A ratios significantly greater than unity. Calculations performed within the framework of the valence bond picture show that the overall electric field gradient at the center of a regular dodecahedron results from two contributions: a negative contribution, associated with the sp^3d^4 σ-bonding orbitals, which is found to be very sensitive to the geometry of the polyhedron, and a positive one arising from the $d_{x^2-y^2}$ π-bonding orbital. As a consequence, the V_{zz} component of the efg tensor tends to turn out positive when the electron-charge density on the $d_{x^2-y^2}$ orbital increases. Similarly, the V_{zz} component calculated by using a point-charge model in D_{2d}-$\bar{4}$ dodecahedra with geometries as close as possible to the actual configurations increases algebraically when Q_B/Q_A goes up: its value is negative for small Q_B/Q_A ratios, vanishes for $Q_B/Q_A \simeq 1.2$, and then becomes positive. As can be seen on Figures 2–4, the same evolution is observed for V_{zz} in real polyhedra, except in the range where fast reorientations of the efg tensor take place.

Let us now consider the especially interesting case of $Hf(BPHA)_4$ which presents both the highest Q_B/Q_A values (1.40) and a positive V_{zz} component of the efg tensor. According to the discussion before, one is tempted to interpret this excess of effective charge on B sites as evidence for a significant electron charge donated by the BPHA ligands onto the $d_{x^2-y^2}$ π orbital of the metal. This interpretation is completely consistent with structural data which show that oxygen atoms with better π-donor capability (those of NO groups) are located at the B vertices of the coordination polyhedron.[6] The large difference between hafnium–oxygen distances ($Hf–O_A/Hf–O_B = 1.07$) attests unequivalent $Hf–O_A$ and $Hf–O_B$ bonds. On the other hand, the direction of V_{zz} is expected to coincide more or less with the quasi-$\bar{4}$ axis retained by the HfO_8 coordination group. This prediction is remarkably well verified since the angle between the direction of the quasi-$\bar{4}$ axis and the V_{zz} component calculated for $Q_B/Q_A = 1.40$ is only 8°.

The example of $Hf(BPHA)_4$ suggests that the results obtained for $Hf(cupferrate)_4$ and $Hf(T)_4{\cdot}DMF$ can be interpreted in the same way: Q_B/Q_A ratios within the range 1.13–1.20 could correspond to small but significant charge transfer from symmetrical tropolonate or cupferrate ligands to the central atom via $d_{x^2-y^2}$–π interactions. The case of $Hf(cupferrate)_4$ deserves some comments: the structure of this chelate displays a distance ratio $Hf–O_A/Hf–O_B$ lower than unity and a greater charge donation onto $Hf–O_A$ bonds could be expected to take place.[17] Our results are not in contradiction with this observation but rather mean that the contribution to the electric field gradient of an eventual excess of charge on the $Hf–O_A$ bonds would be overcompensated by the contribution arising from $\pi \rightarrow d_{x^2-y^2}$ donation.

Within the framework of a simple σ–π bonding picture, the V_{zz} component of the efg tensor at the metal site in dodecahedral 5d complexes can be written

$$V_{zz} = {}^4\!/_7 e(1 - R_d)(\eta_\pi - \alpha\bar{n}_\sigma)\langle r^{-3}\rangle_{5d} \qquad (6)$$

In this expression, $\bar{n}_\sigma$ is the average population of each sp^3d^4 σ-bonding orbital, n_π is the population of the $d_{x^2-y^2}$ π-bonding orbital, and α is a positive coefficient depending on the hybridization parameters within the two groups of equivalent σ-bonding orbitals. The populations must satisfy the relation $\Delta q = -e(n_\pi + 8\bar{n}_\sigma)$ where Δq is the overall charge transferred onto the valence orbitals of the d^0 metal ion. As mentioned before, the contribution to V_{zz} of the σ-bonding charge density is strongly dependent on the geometry of the coordination polyhedron. This prevents in general any evaluation of the charge $(-en_\pi)$ donated onto the $d_{x^2-y^2}$ orbital. However, α is found to be rather small (<0.20) for the dodecahedral configurations calculated by Duffey[38] by maximizing the σ-bond energies. In $Hf(BPHA)_4$, the values of the angles θ_A and θ_B between the pseudo-$\bar{4}$ axis and the directions of the $Hf–O_A$ and $Hf–O_B$ bonds, respectively, are on the average very close[6] to the values corresponding to the "best" dodecahedral structure obtained by Duffey. By taking the value $-1.1e$ given in Table II for Δq in $Hf(BPHA)_4$ and assuming $\alpha = 0.20$, we have $\bar{n}_\sigma = {}^1\!/_8(1.1 - n_\pi)$ and then $n_\pi - \alpha\bar{n}_\sigma = 1.02n_\pi - 0.027$. With $\langle r^{-3}\rangle_{5d} = 8.1$ au, $1 - R_d = 0.85$, and $V_{zz} = +1.03 \times 10^{18}$ $V{\cdot}cm^{-2}$ (which corresponds to $\omega_Q = 102.2$ $Mrd{\cdot}s^{-1}$) eq 6 is satisfied for $n_\pi = 0.27$. If α is taken equal to zero, then one finds $n_\pi = 0.25$. Accordingly, it appears that V_{zz} practically arises from the charge density on the $d_{x^2-y^2}$ orbital only, the contribution due to the charge density on the σ-bonding orbitals being quite negligible. Such a result is consistent with the large and positive value found for V_{zz} in $Hf(BPHA)_4$. It is consistent with the rather large Q_B/Q_A ratio given by the point-charge model also. A value of 0.25 for n_π corresponds to a charge on the $d_{x^2-y^2}$ orbital which is about 20% of the overall charge donated by the ligands onto the valence bond orbitals of the metal.[39]

Owing to the quite different π-donor capabilities of the two ligating atoms of the 8-hydroxyquinolinate ligand, the Q_B/Q_A ratio and then the charge donation onto the $d_{x^2-y^2}$ orbital are expected to be still larger for $Hf(8\text{-quin})_4$ than for $Hf(BPHA)_4$. By assuming $\alpha\bar{n}_\sigma$ to be negligible with respect to n_π and V_{zz} to be positive, we note that eq 6 gives $n_\pi \simeq 0.40$ for $Hf(8\text{-quin})_4$. The knowledge of the real atomic positions within the HfO_4N_4 coordination group and the determination of the sign of V_{zz} would be of great interest in order to verify the validity of our assumptions. Another decisive test for the model presented here would be the tetrakis(*N*-ethylsalicylaldiminato)hafnium(IV), the stereochemistry of which supports Orgel's rule[4] with θ_A and θ_B angles very close to those found in $Hf(BPHA)_4$. Unfortunately, as for $Hf(8\text{-quin})_4$, the atomic positions in this chelate are not available.

With $\Delta q \simeq -0.8e$ (see Table II) and $V_{zz} = +0.56 \times 10^{18}$ $v{\cdot}cm^{-2}$, a similar calculation leads to the value $n_\pi \simeq 0.13$ for $Hf(cupferrate)_4$. Accordingly, the charge on the $d_{x^2-y^2}$ orbital is about 16% of the overall charge transferred onto the metal.

This result qualitatively agrees with the fact that the cupferrate ligand is more symmetrical than the BPHA ligand.

As already mentioned, the quadrupole-coupling parameters measured in the two compounds $Na_4Hf(C_2O_4)_4{\cdot}3H_2O$ and $K_4Hf(C_2O_4)_4{\cdot}5H_2O$ have been interpreted by using the same approach.[11] The overall charge donated by the four oxalato ligands onto the valence orbitals of the metal in the $Hf(C_2O_4)_4^{4-}$ anion was found to be roughly $-2e$. Such a value corresponds to an average ionicity of 50% for the hafnium–oxygen bonds, in agreement with the conclusions reached from infrared spectroscopy experiments.[36] This result must be connected with the significant dissymmetry observed in C–O distances within the $C_2O_4^{2-}$ ligand: whereas the four C–O bonds are equivalent in the free $C_2O_4^{2-}$ ion,[40] the two C–O bonds coordinated to the metal are lengthened, and the other two are shortened in the $Hf(C_2O_4)_4^{4-}$ (or isomorphous $Zr(C_2O_4)_4^{4-}$) anion,[41,42] which is an indication for strong hafnium–oxygen interactions. According to our results, the charge donation would be noticeably lower in the three chelates $Hf(NBPHA)_4$, Hf(cupferrate), and $Hf(T)_4$ than in the tetrakis(oxalato)hafniate anion. Values between $-0.8e$ and $-1.2e$ for the total charge transferred onto the central ion suggest that the hafnium–oxygen interactions are greatly dominated by electrostatic forces in these neutral eight-coordinate d^0 complexes.

Registry No. $Hf(BPHA)_4$, 66673-11-8; $Hf(cupferrate)_4$, 38356-62-6; $Hf(T)_4$, 12367-98-5; $Hf(T)_4{\cdot}DMF$, 61977-48-8; $Hf(8\text{-quin})_4$, 21392-78-9.

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ENDOR Studies of [*N,N'*-Ethylenebis(salicylideniminato)]copper(II) in [*N,N'*-Ethylenebis(salicylideniminato)]nickel(II) Single Crystals

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ENDOR spectra of [*N,N'*-ethylenebis(salicylideniminato)]copper(II) doped in [*N,N'*-ethylenebis(salicylideniminato)]nickel(II) single crystals are reported. Nitrogen hyperfine couplings, eight proton hyperfine couplings within the molecule, and five proton hyperfine couplings due to the neighboring molecules were determined. The quadrupole coupling tensor of the nitrogen nuclei was also obtained. From comparison with ligand hyperfine interactions for related copper(II) complexes, it is shown that the Cu–N bonds in [*N,N'*-ethylenebis(salicylideniminato)]copper(II) have a stronger covalency than that of copper(II) complexes with a trans N–Cu–N configuration, while Cu–O in the former has less covalency than in the latter complexes. The presence of a correlation between the orbital hybridization of the coordinating atoms and spin distribution in the ligands is also suggested. The electron populations on the nitrogen orbitals were evaluated from the quadrupole coupling tensor.

Introduction

For investigations of the nature of metal–ligand bonding in paramagnetic metal complexes, observation of superhyperfine interactions of ligand nuclei is useful. ENDOR is effective for the ligand hyperfine interaction and determination of the coupling constants with high accuracy.[1] In the present work, [*N,N'*-ethylenebis(salicylideniminato)]copper(II), Cu(salen), in a single-crystal form doped into [*N,N'*-ethylenebis(salicylideniminato)]nickel(II), Ni(salen), has been examined by ENDOR spectroscopy. Though there have been several investigations of Schiff base complexes of copper(II) in single-crystal forms,[1e,f,2] we aimed to obtain more detailed information on

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