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Article

Molecular Structures of Tris(dipivaloylmethanato) Complexes of the Lanthanide Metals, Ln(dpm)$_3$, Studied by Gas Electron Diffraction and Density Functional Theory Calculations: A Comparison of the Ln–O Bond Distances and Enthalpies in Ln(dpm)$_3$ Complexes and the Cubic Sesquioxides, Ln$_2$O$_3$

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The molecular structures of tris(dipivaloylmethanato)neodymium(III), Nd(dpm)$_3$, and tris(dipivaloylmethanato)ytterbium(III), Yb(dpm)$_3$, have been determined by gas electron diffraction (GED) and structure optimizations through density functional theory (DFT) calculations. Both molecules were found to have D_3 molecular symmetry. The most important structure parameters (r_a structure) are as follows (GED/DFT): Nd–O = 2.322(5)/2.383 Å, Yb–O = 2.208(5)/2.243 Å, O–Nb–O = 72.1(3)/71.3°, and O–Yb–O = 75.3(2)/75.8°. The twist angles of the LnO$_6$ coordination polyhedron, defined as zero for prismatic and 30° for antiprismatic coordination, were $\theta = 19.1(3)/14.2°$ for Nd and 20.4(2)/19.2° for Yb. Structure optimizations of La(dpm)$_3$, Gd(dpm)$_3$ Er(dpm)$_3$, and Lu(dpm)$_3$ by DFT also yielded equilibrium structures of D_3 symmetry with bond distances of La–O = 2.438 Å, Gd–O = 2.322 Å, Er–O = 2.267 Å, and Lu–O = 2.232 Å. The Ln–O bond distances in 12 Ln(dpm)$_3$ complexes studied by GED decrease in a nearly linear manner with the increasing atomic number (Z) of the metal atom, as do the Ln–O bond distances in the cubic modifications of 14 sesquioxides, Ln$_2$O$_3$. The bond distances in the dpm complexes are, however, about 2% shorter. The mean Ln–O bond rupture enthalpies of the cubic sesquioxides calculated from thermodynamic data in the literature vary in an irregular manner with the atomic number; the La–O, Gd–O, Tb–O, and Lu–O bonds are nearly equally strong, and the remaining bonds are significantly weaker. The Ln–O bond rupture enthalpies previously reported for 11 Ln(dpm)$_3$ complexes are on the average 13 kJ mol^{-1} or about 5% smaller than in the sesquioxides, but they vary in a similar manner along the series: it is suggested that the pattern reflects variations in the absolute enthalpies of the gaseous Ln atoms.

Introduction

The trinitrates of lanthanum and each of the fourteen lanthanide metals from Ce to Lu react with dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptadion) to form the trisdipivaloylmethanates, Ln(dpm)$_3$.[1−3] These complexes form air-stable solids at room temperature, and the combination of thermal stability and high volatility make them suitable for the production of thin films by chemical vapor deposition (CVD) techniques.[4−7]

While the complexes of the first eight elements in the series, from La to Gd, form monoclinic crystals on condensation from the vapor phase or from *n*-hexane, those of the

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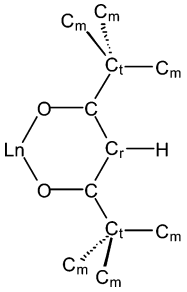
10.1021/ic060079u CCC: $33.50

Scheme 1



last five, from Ho to Lu, form orthorhombic crystals.[8,9] The complexes of the intermediate metals Tb ($Z = 65$) and Dy ($Z = 66$) form monoclinic crystals from hexane solutions and orthorhombic crystals when condensed from the gas phase.[8,9]

X-ray investigations of the orthorhombic crystal structures of two late lanthanide metal complexes, Er(dpm)$_3$ and Lu(dpm)$_3$, have shown that they are monomeric in the solid phase.[10,11] As expected, the structures of the two complexes were found to be very similar. The molecules occupy crystal sites of mirror symmetry with the six atoms of one metal−ligand ring LnO_2C_3 lying in the symmetry plane, Scheme 1. The two remaining metal−ligand rings were also planar, although this is not required by the space group symmetry. The orientation of the *tert*-butyl groups were such that one of the C_t-C_m bonds eclipsed a $C-C_r$ bond in the ligand ring. The six oxygen atoms were found to form a near-perfect trigonal prism, and the molecules were found to have approximate D_{3h} symmetry.

An X-ray investigation of the monoclinic crystal structure of an the early lanthanide complex, Pr(dpm)$_3$, has shown that the complex is dimeric in the solid state:[12] one O atom in each monomer unit forms an additional bond to the metal atom of the other. Each of the two metal atoms is thus seven-coordinate. The greater propensity for the formation of dimers among complexes of the earlier lanthanide metals is presumably the result of their larger atomic or ionic radii.

The first gas-phase structure of a lanthanide trisdipivaloylmethanate complex (viz., Er(dpm)$_3$) determined by gas electron diffraction (GED) was published by Shibata and coworkers more than thirty years ago.[13] The Er−O bond distance and the geometry of the dpm ligands were not significantly different from those found in the crystalline phase, but the overall shape and symmetry of the complex differed in two important respects. In the gas phase, the symmetry of the O_6 coordination polyhedron was D_3 rather than D_{3h}, and the ErO_2C_3 rings were folded along the O⋯O vector, the dihedral angle between the ErO_2 and O_2C_3 planes being $\upsilon = 22.2(15)°$. This folding reduces the molecular symmetry from D_3 to C_3.

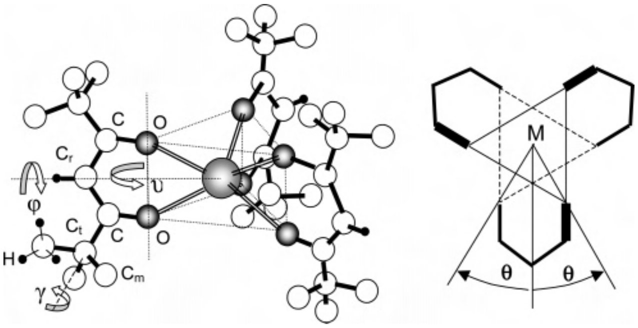


Figure 1. (left) Molecular model of a Ln(dpm)$_3$ complex with D_{3h} symmetry. (right) A molecular model with D_3 symmetry may be formed by rotating the triangle formed by the three upper O atoms through an angle θ in the clockwise direction, and the triangle formed by the lower O atoms through the same angle in the anticlockwise direction. In a D_3 model, the pitch angle, φ (or the angle of rotation of the ligand rings about the $Ln-C_r$ vector), is defined as the angle between the C_3 symmetry axis and the LnO_2 plane of a metal−ligand ring. The folding angle, υ, of an LnO_2C_3 ring in a complex of C_3 symmetry is defined as the angle between the LnO_2 and the O_2C_3 planes. The angle of rotation of the *tert*-butyl groups, γ, is defined as zero when a C_t-C_m bond is eclipsing the $C-C_r$ bond.

The structure of an O_6 coordination polyhedron of D_3 symmetry is completely determined by three independent structure parameters, for instance the Ln−O bond distance, the O⋯O distance across the metal−ligand rings, commonly referred to as the ligand bite, and finally the twist angle, θ, or the pitch angle, φ. For the definitions of θ and φ, see Figure 1. If the coordination polyhedron is trigonal prismatic, θ and φ are both equal to zero, and if it is antiprismatic, $\theta = 30°$.

According to Shibata and co-workers, gaseous Er(dpm)$_3$ was characterized by a twist angle, θ, of about 11° and a pitch angle of about 13°. During the year that followed, they published the results of GED studies of seven more Ln(dpm)$_3$ complexes with Ln = Pr, Sm, Eu, Gd, Tb, Dy, and Ho.[14,15] All were found to have gas-phase structures of C_3 symmetry similar to that of Er(dpm)$_3$ with folding angles, υ, ranging from 14 to 28° and twist angles, θ, ranging from 4 to 12°.

Kepert has developed a simple, but effective, model for the prediction of the structures of the coordination polyhedron in metal complexes.[16] According to this model, the shape of the polyhedron is determined by repulsion between the electron densities of the bonds between the metal and ligating atoms. The repulsion energy for a pair of bonds is calculated as

$$u_{ij} = a/d_{ij}^{\,n}$$

where a is a constant, d_{ij} is the distance between the effective centers of bond charges, and the exponent n is normally

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assumed to be $n = 6$. If all bonds are chemically equivalent, the effective centers of the bond charges are all at the same distance from the metal atom, and the total repulsion energy, calculated as the sum-over pair-repulsion energies, is completely determined by the angular distribution of the bonds. For a complex of the Ln(dpm)$_3$ type with three identical bidentate ligands of C_2 symmetry, the total repulsion energy is found to be at a minimum if the coordination polyhedron has D_3 symmetry, while the magnitude of the twist angle, θ, is determined by the ratio between the O···O and Ln−O distances, $b = r(\mathrm{O}\cdots\mathrm{O})/r(\mathrm{Ln{-}O})$, which Kepert refers to as the "normalized bite". If $b = \sqrt{2}$ (i.e., if the two chelating O atoms span a valence angle of 90°), θ is calculated to be 30° corresponding to an antiprismatic coordination polyhedron. If the valence angle (and hence, the normalized bite) is reduced, the twist angle decreases toward 0° corresponding to a trigonal prism.

A survey of the crystal structures of 158 main group and transition metal complexes with three identical bidentate ligands and normalized bites ranging from 1.07 to 1.50 showed that Kepert's bond repulsion model reproduced the observed twist angles in all but 11 complexes with an accuracy of better than 5°.[17] The model appears, however, to fail for Ln(dpm)$_3$ complexes. The structures reported by Shibata and co-workers are characterized by normalized bites ranging from 1.16 to 1.22 and twist angles ranging from 4 to 12°, while Kepert's repulsion model predicts twist angles ranging from 17 to 21°.

Three or four years ago, we reported the results of a GED study on La(dpm)$_3$.[18] The structure refinement under C_3 symmetry yielded a folding angle very close to zero, indicating that the molecular symmetry is D_3 rather than C_3. The normalized bite was found to be 1.17 and the twist angle was found to be 23(2)°, in reasonable agreement with the value predicted by Kepert's model ($\theta = 19°$). During a recent reinvestigation of Er(dpm)$_3$ by GED, we identified *two* minima on the square-error surface, the higher minimum with folding and twist angles similar to those reported by Shibata and co-workers and the lower with a folding angle close to zero and a twist angle of $\theta = 20.7(8)°$, twice as large as that obtained in the earlier study.[19] Very recently, we published the result of a combined GED and computational study of Lu(dpm)$_3$.[20] Structure optimization by DFT calculations yielded an equilibrium model with planar LuO$_2$C$_3$ rings and overall D_3 symmetry; the least-squares structure refinements under C_3 symmetry yielded a folding angle not significantly different from zero and a twist angle of $\theta = 22.2(15)°$, in reasonable agreement with the ones obtained by DFT calculations (19.5°) or predicted by Kepert's model (22°).

Table 1. Gas Electron Diffraction (GED) Data Collection[a]

	Nd(dpm)$_3$		Yb(dpm)$_3$	
nozzle-to-plate distance (mm)	338	598	338	598
electron beam current (μA)	1.17	0.85	1.28	1.11
accelerating potential (kV)	64	64	64	64
effusion cell temperature[b] (°C)	165(5)	158(5)	122(5)	120(5)
exposure time (s)	135−150	75	120−140	60−90
residual gas pressure (mbar)	2.5×10^{-6}	2.5×10^{-6}	5.0×10^{-6}	4.8×10^{-6}

[a] Kodak Electron Image film. [b] Measured by a W−Re-5/20 thermocouple standardized by the melting points of Sn and Al.

Table 2. Synchronous Mass Spectra[a]

	Nd(dpm)$_3$		Yb(dpm)$_3$	
ion	m/z^b	abundance (%)	m/z^b	abundance (%)
$[\mathrm{Ln(dpm)_3}]^+$	693(693)	17.5	722(725)	28.4
$[\mathrm{Ln(dpm)_3} - \mathrm{C(CH_3)_3}]^+$	636(636)	63.7	665(668)	100
$[\mathrm{Ln(dpm)_2}]^+$	510(510)	100	539(542)	89.5
$[\mathrm{Ln(dpm)_2} - \mathrm{CH_3}]^+$	495(495)	7.3	524(527)	7.5
$[\mathrm{Ln(dpm)_2} - \mathrm{C(CH_3)_3}]^+$	453(451)	4.1	482(483)	5.3
$[\mathrm{Ln(dpm)}]^+$	327(325)	4.7	356(357)	26.2
$[\mathrm{Ln(dpm)} - \mathrm{C(CH_3)_3}]^+$	270(268)	10.9	299(300)	12.0

[a] Ionizing potential 50 V. [b] The values measured during synchronous GED/MS experiment are given in brackets (the accuracy is ±3 amu).

In this article, we report (i) the molecular structures of Nd(dpm)$_3$ and Yb(dpm)$_3$ determined by synchronous GED and mass spectrometric experiments; (ii) the molecular structures of Ln(dpm)$_3$, Ln = La, Nd, Gd, Er, Yb, or Lu, determined by DFT structure optimizations; and (iii) a comparison of the length and strength of the Ln−O bonds in Ln(dpm)$_3$ complexes and in the solid cubic sesquioxides, Ln$_2$O$_3$.

Experimental and Computational Section

Gas Electron Diffraction. Samples of Nd(dpm)$_3$ and Yb(dpm)$_3$ were synthesized as described in ref 21 and characterized by elemental analysis. The mass spectra of superheated vapors were recorded over a wide temperature range to find the optimal conditions for the GED experiment. MS spectra recorded at temperatures below 300 °C indicated the presence of monomeric species only. Thermal decomposition was observed from about 350 °C, and metal-containing ions disappeared from the mass spectrum at about 660 (Ln = Nd) or 730 °C (Ln = Yb). GED data and mass spectra were recorded simultaneously[22,23] with a molybdenum effusion cell. Experimental conditions are summarized in Table 1. The electron wavelength was calibrated using polycrystalline ZnO. The relative abundances of the characteristic ions are listed in Table 2. The optical densities of exposed films were recorded on a computer-controlled MD-100 (Carl Zeiss, Jena, Germany) unit.[24] The background functions, $G(s)$, were refined by the Fourier spectrum analysis of the intensity curves, $I_{\mathrm{obs}}(s)$.

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Table 3. Root-Mean-Square Amplitudes of Vibrations (l_{calcd}) and Vibrational Correction Terms ($d_{calcd} = r_\alpha - r_a$) Calculated from the Molecular Force Fields of Nd(dpm)$_3$ and Yb(dpm)$_3$ and the Amplitudes of Vibrations (l_{GED}) Obtained by Least-Squares Calculations to the GED Data[a]

	Nd(dpm)$_3$		Yb(dpm)$_3$	
	l_{calcd}/l_{GED}	d_{calcd}	l_{calcd}/l_{GED}	d_{calcd}
Ln−O	0.076/0.066(3)	−0.0070	0.071/0.079(3)	−0.0058
O−C	0.043/0.052(2)	−0.0055	0.042/0.046(3)	−0.0044
C−C$_r$	0.047/0.050(2)	−0.0095	0.047/0.040(2)	−0.0083
C−C$_t$	0.048/0.051(2)	−0.0226	0.048/0.058(2)	−0.0202
C$_t$−C$_m$	0.051/0.060(2)	−0.0147	0.051/0.050(2)	−0.0118
C$_m$−H	0.079/0.085(2)	−0.0161	0.079/0.100(3)	−0.0249
Ln···C	0.079/0.099(3)	−0.0089	0.073/0.123(6)	−0.0062
Ln···C$_r$	0.100/0.094(11)	−0.0057	0.092/0.110(6)	−0.0045
Ln···C$_t$	0.091/0.120(9)	−0.0217	0.084/0.084(7)	−0.0167
O···O[b]	0.123/0.110(3)	−0.0024	0.114/0.115(3)	−0.0017
O···O[c]	0.178/0.252(3)	0.0027	0.163/0.162(6)	0.0023
O···O[d]	0.154/0.224(3)	−0.0016	0.138/0.217(6)	−0.0013
O···O[d]	0.109/0.061(9)	−0.0035	0.101/0.081(7)	−0.0027

[a] All parameters in angstroms. Estimated uncertainties of GED amplitudes are given as 2.5σ_{LS}, where σ_{LS} is the standard deviation obtained by least-squares refinement. [b] Distance between O atoms in the same ligand ring. [c] Distance between O atoms in different rings related through the C_3 symmetry axis. [d] Distance between O atoms in different rings related through a C_2 symmetry axis.

Structure Refinements. Least-squares structure refinements were based on molecular models of C_3 symmetry. The LnO$_6$ coordination polyhedron were assumed to have D_3 and the dpm ligands to have C_2 symmetry. Both the methyl and *tert*-butyl groups were assumed to have local C_{3v} symmetry. The structure of the models was described by fourteen independent parameters (i.e., the six bond distances, Ln−O, O−C, C−C$_r$, C−C$_t$, C$_t$−C$_m$, and C$_m$−H, the five valence angles, O−Ln−O, inside the chelate ring, C−C$_r$−C, O−C−C$_t$, C−C$_t$−C$_m$, and C$_t$−C$_m$−H, the pitch angle, φ, of the ligand rings, the dihedral angle, γ, determining the orientation of the *tert*-butyl groups, and the folding angle of the LnO$_2$C$_3$ rings, υ. The twist angle, θ, is thus refined as a dependent parameter. The C$_r$−H bond distance was fixed at the calculated value, 1.074 Å. The contribution to the molecular intensity from H···H and C···H atom pairs belonging to different *t*-butyl groups were neglected.

Exploratory structure refinements based on geometrically consistent r_a models led to the identification of *two* least-squares minima for each compound. Root-mean-square vibrational amplitudes (l) and vibrational correction terms ($d = r_\alpha - r_a$) were calculated for the geometry corresponding to each minimum by the methods described in refs 25 and 26. The force constants for the LnO$_6$ cores were estimated to be f(Ln−O) = 1.15 and 1.5 mdyn/Å, f(O−Ln−O) = 0.076 and 0.082 mdyn/Å, f(Ln−O−C) = 0.17 and 0.17 mdyn/Å, f_{tors}(LnO) = 0.17 and 0.18 mdyn/Å, and f(O−Ln−O′) = 0.038 and 0.041 mdyn/Å, for Ln = Nd and Yb, respectively. Other force constants were assumed equal to those of Y(dpm)$_3$.[27] The amplitudes and correction terms thus obtained are listed in Table 3. Finally the structure refinements were repeated with geometrically consistent r_α models. The R factors obtained for the best models

$$R_f = \sqrt{[\sum w(s)[sM_{exptl}(s) - sM_{calcd}(s)]^2/\sum w(s)(sM_{exptl})^2]}$$

were 0.0307 for Ln = Nd and 0.0305 for Ln = Yb. The structure parameters of the best models are listed in Table 4, and the values of refined vibrational amplitudes are given in Table 3. The experimental and theoretical radial distribution curves, $f(r)$, are compared in Figure 2.

Quantum Chemical Calculations. All quantum chemical calculations were carried out with the Gaussian 98 suite of programs.[28] The molecular structures of Ln(dpm)$_3$, Ln = La, Nd, Gd, Er, Yb, or Lu, were optimized by DFT calculations under D_3 symmetry using the standard B3LYP functional which is based on Beckes's three-parameter hybrid method[29] in combination with the Lee−Yang−Parr correlation functional.[30] The large core RECPs basis set (MWB) developed by the Stuttgart group was used for lanthanide atoms.[31] The oxygen, carbon, and hydrogen atoms were described by standard 6-31G* basis sets.[32] Structure optimizations were followed by calculations of the molecular force field to ensure that the structures obtained corresponded to minima on the potential energy surfaces. The net atomic charges in Lu(dpm)$_3$ were estimated by NBO population analyses.[33]

Results and Discussion

Molecular Structures Determined by GED. Structure refinements of Nd(dpm)$_3$ and Yb(dpm)$_3$ based on models of C_3 symmetry led to the identification of two least-squares minima for each compound. For Nd(dpm)$_3$, the R factors associated with the minima were R_f = 3.07 and 4.60% respectively. Nd−O bond distances and O−Nd−O valence angles in the two minima were indistinguishable: Nd−O = 2.322(5) Å and O−Nd−O = 72.1(3)° and Nd−O = 2.324(5) Å and O−Nd−O = 72.0(3)° for the low and high R factor minima, respectively. The values obtained for the folding and twist angles were, however, significantly different: υ = 0.3(15)° and θ = 19.1(3)° and υ = 22.1(7)° and θ = 5.8(2)° for the lowest and highest minima, respectively. For Yb(dpm)$_3$, the R factors were R_f = 3.05 and 4.54%,

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Table 4. Structure Parameters of $\mathrm{Ln(dpm)_3}$ Complexes (Ln = La, Nd, Gd, Er, Yb, or Lu) Determined by Gas Electron Diffraction (GED) and Structure Optimization by Quantum Chemical DFT Calculations[a]

	$\mathrm{La(dpm)_3}$		$\mathrm{Nd(dpm)_3}$		$\mathrm{Gd(dpm)_3}$	$\mathrm{Er(dpm)_3}$		$\mathrm{Yb(dpm)_3}$		$\mathrm{Lu(dpm)_3}$	
	GED[b]	DFT[c]	GED[b]	DFT[c]	DFT[c]	GED[b]	DFT[c]	GED[b]	DFT[c]	GED[b]	DFT[c]
Ln−O	2.379(6)	2.438	2.322(5)	2.383	2.322	2.224(5)	2.267	2.208(5)	2.243	2.192(6)	2.232
C−O	1.284(5)	1.278	1.285(3)	1.279	1.279	1.284(5)	1.280	1.286(3)	1.280	1.270(4)	1.280
$\mathrm{C-C_r}$	1.407(7)	1.410	1.415(4)	1.409	1.409	1.412(6)	1.408	1.416(5)	1.408	1.397(6)	1.408
$\mathrm{C-C_t}$	1.540(5)	1.546	1.530(6)	1.545	1.544	1.533(3)	1.544	1.531(8)	1.543	1.541(3)	1.543
$\mathrm{C_t-C_m}$	1.559(6)	1.544	1.566(4)	1.544	1.544	1.554(5)	1.544	1.551(4)	1.544	1.549(6)	1.544
$\mathrm{C_m-H}$	1.108(5)	1.096	1.082(3)	1.096	1.096	1.109(4)	1.096	1.091(3)	1.096	1.089(6)	1.096
O···O	2.77(3)	2.786	2.728(11)	2.778	2.768	2.701(15)	2.758	2.693(12)	2.755	2.73(2)	2.754
b	1.167(15)	1.143	1.175(6)	1.166	1.192	1.217(6)	1.217	1.222(4)	1.228	1.253(8)	1.234
O−Ln−O	71.4(2)	69.7	72.1(3)	71.3	73.2	75.0(4)	74.9	75.3(2)	75.8	77.6(6)	76.2
$\mathrm{C-C_r-C}$	123.7(13)	124.9	124(2)	124.9	124.7	122.5(15)	124.5	121(2)	124.5	124.1(10)	124.4
$\mathrm{O-C-C_t}$	116.8(7)	114.8	116.8(4)	114.8	114.8	116.1(8)	114.8	115.2(7)	114.8	115.7(10)	114.8
$\mathrm{C-C_t-C_m}$	109.5(5)	109.7	109.2(3)	109.8	109.8	108.6(5)	109.7	110.8(3)	109.7	109.6(7)	109.7
$\mathrm{C_t-C_m-H}$	109.0(4)	110.8	104.6(5)	110.8	110.8	109.3(11)	110.8	109.5(6)	110.8	110.6(12)	110.8
φ	35.6(13)	8.6	28.4(4)	20.7	23.1	29.4(11)	25.4	28.8(5)	26.6	30.5(17)	26.9
θ	23(2)	5.9	19.1(3)	14.2	16.9	20.7(8)	18.2	20.4(2)	19.2	22.2(15)	19.5
γ	9(3)	0.5	4.6(12)	0.5	0.9	12.7(11)	0.2	9.1(8)	0.5	22(2)	0.6
υ	3.0(14)	0	0.3(15)	0	0	2.2(15)	0	1.9(15)	0	2.0(5)	0
E		−1775.1		−1777.0	−1779.4		−1781.8		−1782.9		−1783.5

[a] Interatomic distances in angstroms, angles in degrees, and energy in Hartree. The normalized bite $b = r(\mathrm{O\cdots O})/r(\mathrm{Ln\text{-}O})$. For definitions of the angles θ, φ, γ, and υ, see Figure 1. [b] The uncertainties of interatomic distances (r_a) are given as $\sigma = \sqrt{[(0.002r)^2+\sigma_{LS}^2]}$, and the uncertainties of angles ($\angle_\alpha$) are given as $2.5\sigma_{LS}$. [c] Equilibrium interatomic distances and angles.

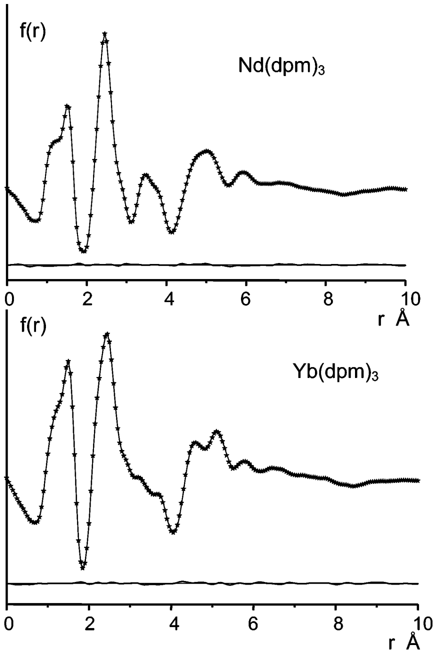

Figure 2. Experimental and difference (experimental − theoretical) radial distribution curves for $\mathrm{Nd(dpm)_3}$ and $\mathrm{Yb(dpm)_3}$. The artificial damping constants, k, are 0.0035 and 0.0042 Å^2.

respectively. Yb−O bond distances and O−Yb−O valence angles in the two minima were indistinguishable, but the folding and twist angles were again significantly different: $\upsilon = 1.9(15)°$ and $\theta = 20.4(2)°$ and $\upsilon = 22.3(5)°$ and $\theta = 6.4(2)°$ for the lowest and highest minima, respectively.

Application of Hamilton's R-factor test[34] indicates that the models with the higher R factors may be rejected at the 0.025 significance level, and in the following, we base our discussion on the structure parameters yielding the lower R factor, Table 4. It is seen that the folding angles of the ligands, $\upsilon = 0.3(15)°$ for Nd and $1.9(15)°$ for Yb, are *not* significantly different from zero. The GED data thus provide no indication for ring folding or for deviation from overall D_3 molecular symmetry. This conclusion is in agreement with the results obtained in our earlier studies of $\mathrm{Er(dpm)_3}$, $\mathrm{La(dpm)_3}$, and $\mathrm{Lu(dpm)_3}$.

Before continuing, we pause to note that the values of the folding and twist angles corresponding to the highest minima are very similar to those reported in the early GED studies of $\mathrm{Pr(dpm)_3}$, $\mathrm{Sm(dpm)_3}$, $\mathrm{Eu(dpm)_3}$, $\mathrm{Gd(dpm)_3}$, $\mathrm{Tb(dpm)_3}$, $\mathrm{Dy(dpm)_3}$, $\mathrm{Ho(dpm)_3}$, and $\mathrm{Er(dpm)_3}$.[13−15]

Structure Optimizations by DFT Calculations. Maron and Eisenstein have investigated the role of the f electrons in the metal−ligand bonding of the trisamides $\mathrm{Ln(NH_2)_3}$ for all metals in the series from La to Lu except Ce, Eu, and Yb using quantum chemical density functional theory (DFT) calculations with relativistic effective core potential (RECP) basis sets.[35] Calculations were carried out with small and large atomic cores: small cores included the 28 electrons in the $n = 1$, 2, or 3 orbitals, and the electrons in the $n = 4$, 5, or 6 orbitals were treated explicitly. Calculations with the small-core basis sets showed that the metal atoms carry net positive charges close to three, so that the number of f electrons corresponded to that of the free $\mathrm{Ln^{3+}}$ ions and the ground state f electron configurations were high spin as suggested by Hund's rule. These results indicate that the f electrons do not participate in the bonding. The large cores also included the $n = 4$ electrons; only the eleven electrons occupying the 5s, 5p, 5d, or 6s orbitals in the tripositive ions $\mathrm{Ln^{3+}}$ were treated explicitly. Structure optimizations with the large-core basis sets yielded Ln−N bond distances which

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(34) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

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were on the average 0.04 Å longer than those obtained with the small-core basis set.

Structure optimizations of the six $Ln(dpm)_3$ complexes with Ln = La, Nd, Gd, Er, Yb, or Lu under D_3 symmetry using the same large core RECP basis sets[31] yielded the structure parameters listed in Table 4. Calculations of the force constant matrix confirmed that these structures represent minima on the potential energy surface. The conclusions reached in our GED investigations regarding the symmetry of the La, Nd, Er, Yb, and Lu complexes were thus confirmed by the calculations.

It seems clear that the authors of the early GED study of $Er(dpm)_3$ must have overlooked the second, deeper minimum on the square-error surface of the compound. The same authors investigated $Gd(dpm)_3$ and concluded that the GdO_2C_3 rings were folded and the molecular symmetry was C_3. Our DFT calculations, on the other hand, indicate that the equilibrium structure has planar rings and D_3 symmetry. We consider it probable that *all* complexes in the $Ln(dpm)_3$ series have gas-phase molecular structures of D_3 symmetry similar to those the La, Nd, Gd, Er, Yb, or Lu complexes, that GED investigations of all complexes would yield double-minimum square-error surfaces similar to those found for the Nd, Er, and Yb compounds, and that the authors of the early investigations of $Ln(dpm)_3$ complexes by GED, who did not have calculated amplitudes or vibrational correction terms at their disposal, missed the second and deeper minimum.

An inspection of Table 4 shows that there is reasonable agreement between the experimental and calculated bond distances and valence angles. The calculated Ln−O bond distances are on the average 0.043 Å or about 2% longer than their experimental counterparts. The lanthanide contraction, defined as the difference between the La−O and Lu−O bond distances, is 0.187(12) Å by GED and 0.206 Å by DFT calculations. The calculated ligand bite decreases from 2.786 Å in $La(dpm)_3$ to 2.754 Å in $Lu(dpm)_3$; this difference is too small to be detected by GED. The decreasing bond distance, however, leads to a significant increase of the normalized bite, b, which according to Kepert's model should lead to an increase of the twist angle, θ, and indeed, the calculated twist angles increase monotonically from 5.9° in $La(dpm)_3$ to 19.5° in $Lu(dpm)_3$. The former is closer to a trigonal prismatic coordination geometry, while the latter is closer to trigonal antiprismatic. The experimental twist angles fall in a very narrow range from 19 to 23°. Except for $La(dpm)_3$, they are in reasonable agreement with experiment.

A D_3 complex may be converted into its optical isomer by concerted rotation of all ligand rings about their 2-fold symmetry axes. The activation energy (i.e., the energy of the prismatic D_{3h} transition state relative to the equilibrium structure) would presumably be higher the closer the latter is to a trigonal antiprism, and indeed, the calculation on the $Ln(dpm)_3$, Ln = La or Lu, indicates that the relative energy of the transition state increases from about 1 kJ/mol for $La(dpm)_3$ to about 10 kJ/mol for $Lu(dpm)_3$. Given the small energy differences between the D_{3h} transition states and the D_3 equilibrium structures in the gas phase, it is not surprising that $Er(dpm)_3$ and $Lu(dpm)_3$ are found to have D_{3h} symmetry in the crystalline phase.[10,11]

Electron density maps obtained by ab initio calculations indicate that the bonding between the metal and oxygen atoms in metal β-diketonates is predominantly ionic.[36] NBO analysis for $Lu(dpm)_3$ at the B3LYP/MWB,6-31G* level gave a net charge of +2.1 at Lu, reasonably close to the ionic limit of +3. If one considers the formation of the complex from the ions

$$Ln^{+3}(g) + 3(dpm)^{-1}(g) = Ln(dpm)_3(g)$$

bond formation is accompanied by back-donation of a charge corresponding to about 0.2 of an electron from each ligand. The net charges on the atoms in the chelating ligands are found to alternate between negative and positive: −0.8 (O), +0.6 (C), −0.5 (C_r), +0.6 (C), −0.8 (O).

Comparison of the Ln−O Bond Length and Bond Strength in $Ln(dpm)_3$ Complexes and in the Crystalline Sesquioxides. The sesquioxides Ln_2O_3 crystallize in hexagonal, monoclinic, or cubic space groups.[37] In the hexagonal and monoclinic modifications, the metal atoms (or ions) are seven-coordinate, and in the cubic modification, they are six-coordinate. Not surprisingly, the thermodynamically most stable forms of the oxides of the later lanthanides from Tb to Lu are cubic, while the hexagonal or monoclinic modifications are the most stable for La and the early lanthanide elements from Ce to Gd. The unit cell dimensions of the cubic modifications are, however, known for all members of the series except Pm_2O_3. Each Ln atom is surrounded by six oxygen atoms at the corners of a distorted octahedron, and the average Ln−O distance is equal to 0.21441a, where a is the unit cell dimension.[38] The average Ln−O bond distances calculated from unit cell dimensions in the literature[39] are listed in Table 5. A plot of the variation along the series shows that, with the exception of Ce_2O_3, the bond distances decrease in a nearly linear manner with the increasing atomic number of the metal atom, Figure 3.

A comparison of the structures corresponding to the two minima on the square-error surface found by GED refinements of $Nd(dpm)_3$ and $Yb(dpm)_3$ show that the values obtained for the Ln−O bond distances within the uncertainty limits are independent of the magnitude of the folding angle, υ, and of the type of the structure (r_a or r_α) used for the geometry constraining. The bond distances obtained in the early GED studies of the $Ln(dpm)_3$ complexes may therefore be accepted without reservations. The Ln−O bond distances in the twelve complexes studied by GED up to now are listed in Table 5, and their variation along the series from La to Lu is shown in Figure 3. It can be seen that the Ln−O bond

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(38) Templeton, D. H.; Dauben, C. H. *J. Am. Chem. Soc.* **1954**, *76*, 5237.

(39) The bond distances have been calculated from the unit cell dimensions listed in Villars, V.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*; American Society for Metals: Materials Park, OH, 1985.

Table 5. Ln−O Bond Distances and Mean Bond Rupture Enthalpies in Gaseous Ln(dpm)$_3$ Complexes and in Crystalline Cubic Ln$_2$O$_3$[a]

		Ln(dpm)$_3$ (g)		Ln$_2$O$_3$ (crystalline, cubic)			Ln (g)	
Ln	Z	r(Ln−O)[b]	D(Ln−O)[c]	r(Ln−O)[d]	D(Ln−O)[e]	$\Delta_f H^\circ_m$[f]	$\Delta_f H^\circ$[g]	∑IE[h]
La	57	2.379(6)	280 ± 10	2.429	282 ± 3	−1765 ± 29	431	3474
Ce	58			2.386	282 ± 3	−1792 ± 26	423	3548
Pr	59	2.331(7)	265 ± 10	2.389	271 ± 2	−1795 ± 18	356	3650
Nd	60	2.322(5)	253 ± 10	2.376	267 ± 2	−1798 ± 12	328	3705
Pm	61							
Sm	62	2.278(7)	234 ± 10	2.342	249 ± 1	−1827 ± 5	205	3893
Eu	63	2.271(7)		2.321	230 ± 1	−1663 ± 6	175	4055
Gd	64	2.258(8)	268 ± 10	2.318	281 ± 1	−1827 ± 4	397	3765
Tb	65	2.248(8)	266 ± 10	2.301	283 ± 1	−1865 ± 6	389	3808
Dy	66	2.242(7)		2.284	266 ± 1	−1863 ± 5	290	3915
Ho	67	2.226(8)	253 ± 10	2.274	269 ± 1	−1883 ± 8	301	3942
Er	68	2.224(5)	254 ± 10	2.261	273 ± 1	−1900 ± 7	317	3951
Tm	69		235 ± 10	2.248	258 ± 1	−1889 ± 6	232	4065
Yb	70	2.208(5)	222 ± 10	2.237	239 ± 1	−1815 ± 6	152	4215
Lu	71	2.192(6)	287 ± 10	2.227	290 ± 1	−1877 ± 8	428	3902

[a] Standard enthalpies of formation of cubic Ln$_2$O$_3$ and gaseous Ln atoms and the sum of the first three ionization enthalpies of Ln(g). Bond distances in angstroms and enthalpies in kilojoules per mole. [b] Data from refs 13−15, 18−20, and this work. [c] Data from refs 43−46. [d] See text. With the exception of Pr−O these distances are believed to be accurate to the nearest 0.002 Å. [e] See text. [f] See ref 40. [g] Data from ref 48. They are belived to be accurate to better than 1 kJ mol^{-1}. [h] Data from ref 48.

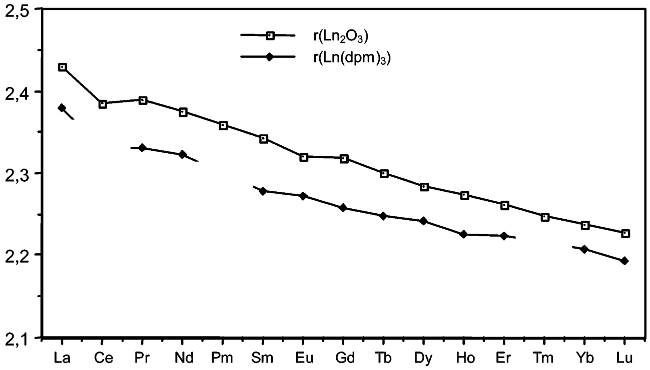

Figure 3. Variation of the Ln−O bond distances in crystalline cubic Ln$_2$O$_3$ and in the gaseous Ln(dpm)$_3$ complexes.

distances in the complexes decrease in the same regular manner as in the sesquioxides. This regularity may be interpreted as another indication that f electrons do not contribute to the bonding. The Ln−O bond distances in the complexes are, however, slightly, but significantly, shorter than in the cubic sesquioxides, the average difference being 0.048 Å or about 2%.

The mean Ln−O bond rupture enthalpy of a cubic sesquioxide may be calculated as one twelfth of the standard enthalpy of the reaction

$$\mathrm{Ln_2O_3(cubic)} = 2\mathrm{Ln(g)} + 3\mathrm{O(g)}$$

$$D(\mathrm{Ln{-}O, Ln_2O_3}) = [2\Delta_f H^\circ(\mathrm{Ln(g)}) + 3\Delta_f H^\circ(\mathrm{O(g)}) - \Delta_f H^\circ(\mathrm{Ln_2O_3})]/12$$

The standard enthalpies of formation of all the cubic sesquioxides,[40] except for Pm$_2$O$_3$, and of the metal atoms are listed in Table 5, along with the resulting mean bond enthalpies.[43] A plot of their variation along the series is shown in Figure 4. The La−O and Lu−O bonds are of very nearly equal strength, but the variation between is irregular; in particular, there is a marked increase of the bond strength between Eu and Gd and between Yb and Lu.

Konings and Kovacs have recently noted a similar variation of the Ln−X bond enthalpies in gaseous lanthanide(III) halides.[44]

Airoldi and co-workers[45−47] have determined the standard enthalpies of formation of 11 Ln(dpm)$_3$ complexes in the gas phase and calculated the mean Ln−O bond enthalpy in

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(40) Corfunke and Konings have recently reviewed the available information on the enhalpies of formation of the most stable forms of the sesquioxides Ln$_2$O$_3$ where Ln = La−Lu.[41] Their recommended values for $\Delta_f H^\circ$ for the cubic modifications of the oxides for all the metals from Sm to Lu except Gd are listed in Table 5. The value for the Gd oxide has been taken from ref 42. Thermodynamic data from ref 42 make it clear that the $\Delta_f H^\circ$ of the hexagonal form of Eu ($Z = 63$) is higher than that of the cubic; the enthalpy difference, $\Delta\Delta H^\circ$, is $\Delta_f H^\circ$(cubic) − $\Delta_f H^\circ$(hexagonal) = −9 kJ mol^{-1}. For the neighbouring element Sm ($Z = 62$), this difference has risen to −3 kJ mol^{-1}. No information is available for the Pm ($Z = 61$) oxide, but the most stable modifications of the oxides of the metals from Nd ($Z = 60$) to La are known to be the hexagonal. The $\Delta_f H^\circ$ values of the hexagonal forms are given in ref 44, and those of the cubic forms are unknown. Linear extrapolation with Z from Eu to La suggests however that the $\Delta\Delta H^\circ$ correction should increase in steps of 6 kJ mol^{-1} from 3 kJ mol^{-1} for Pm to 27 kJ mol^{-1} for La. The addition of these corrections to the $\Delta_f H^\circ$ values of the hexagonal forms yields the standard enthalpies of formation listed in Table 5. We assume that the uncertainties of the corrections, $\Delta\Delta_f H^\circ$, are of the same magnitude as the corrections themselves, and the error limits for the enthalpies of formation of the cubic forms of Ln$_2$O$_3$, Ln = Nd to La, have been expanded accordingly.

(41) Cordfunke, E. H. P.; Konings, R. J. M. *Thermochim. Acta* **2001**, *375*, 65.

(42) Barin, I. *Thermochemical Data of Pure Substances*; VCH: Weinheim, Germany, 1992.

(43) In ref 46, Airoldi and co-workers list mean Ln−O bond enthalpies calculated in a similar manner from the standard atomization enthalpies of the sesquichlorides in their most stable forms, which in some cases are hexagonal or monoclinic (both with CN = 7) in others cubic (with CN = 6). Even though the coordination numbers differ, they chose to divide the atomization enthalpy by 7 in every case. More seriously, they seem to have overlooked that the atomization of 1 mol of the formula unit involves the rupture of 12 (or 14) Ln−O bonds.

(44) Konings, R. J. M.; Kovacs, A. Thermodynamic Properties of the Lanthanide(III) Halides. In *Handbook on Physics and Chemistry of Rare Earths*; Gschneidner, K. A. Jr., Bunzli, J.-C. G., Pecharsky, V. K., Eds.; Elsevier: Amsterdam, 2003; pp 147−247.

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(47) Santos, L. S.; Petrucelli, G. P., Jr.; Airoldi, C. *Polyhedron* **1999**, *18*, 969.

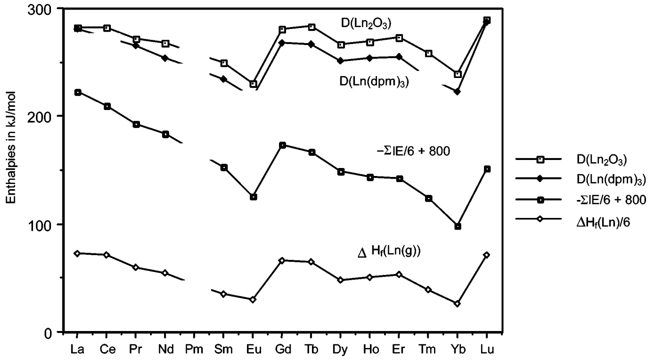

Figure 4. Variation of mean Ln−O bond rupture enthalpies in crystalline cubic Ln_2O_3 and in the gaseous Ln(dpm)$_3$ complexes, the standard enthalpies of formation of the gaseous metal atoms, and the standard enthalpies of the reaction of the gaseous Ln^{+3} ions with 3 electrons to form Ln(g), $\Delta_{\mathrm{neutral}}H°$. Note that the latter is plotted with an offset of 800 kJ mol^{-1} to make the figure more compact.

each as one-sixth of the enthalpy of the reaction

$$\mathrm{Ln(dpm)_3(g) = Ln(g) + 3dpm(g)}$$

$$D(\mathrm{Ln{-}O,\ Ln(dpm)_3}) = [\Delta_f H°(\mathrm{Ln(g)}) + 3\Delta_f H°(\mathrm{dpm}) - \Delta_f H°(\mathrm{Ln(dpm)_3})]/6$$

The resulting values are listed in Table 5, and their variation across the series from La to Lu is displayed in Figure 4. It is seen that the Ln−O bond enthalpies in the complexes are smaller than those in the cubic sesquioxides. The difference between the La−O, Pr−O, and Lu−O bond enthalpies is smaller than the combined uncertainties, but for the metals from Nd to Yb, the differences are significant and average 17 kJ mol^{-1} or about 7%. It is noteworthy that even though the Ln−O bond distances in the complexes are shorter than those in the oxides, the bonds are weaker. The variation of bond enthalpies along the series is, however, seen to be strikingly similar to that of the sesquioxides. In view of the smooth decrease of Ln−O bond distances, we were at first surprised by these irregularities.

In Figure 4 we show the variation of the standard enthalpies of formation of the gaseous atoms divided by six to highlight their contributions to the calculated bond enthalpies. This curve displays the same irregular features as the others. Finally, we used the standard enthalpies of formation of the gaseous atoms and tripositive metal ions[47] to calculate the enthalpy of the reactions

$$\mathrm{Ln^{+3}(g) + 3e(g) = Ln(g)}$$

$$\Delta_r H° = \Delta_f H°(\mathrm{Ln(g)}) - \Delta_f H°(\mathrm{Ln^{+3}(g)}) = -\sum \mathrm{IE}$$

where ∑IE denotes the sum of the first three ionization enthalpies of the metal atoms. The values obtained are listed in Table 5, and the variation of −∑IE/6 along the series is displayed in Figure 4. It can be seen that the enthalpies of the four reactions where a gaseous metal atom is formed from the solid metal, the tripositive ions (and three electrons), the solid sesquioxide (along with O atoms), or the gaseous Ln(dpm)$_3$ (along with dpm radicals) vary in the same irregular manner when plotted against the atomic number. The simplest explanation for the similar irregularities of the four curves would be that they reflect the variation of the absolute enthalpies of the gaseous metal atoms (defined as zero when electrons and nuclei are at infinite distance from each other and at rest), while the absolute enthalpies of solid metals, the gaseous metal ions, the solid sesquioxides, and gaseous Ln(dpm)$_3$ complexes vary in a smooth manner along the series.

Acknowledgment. The financial support of this work was provided by RFBR (Grant 04-03-32661a).

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