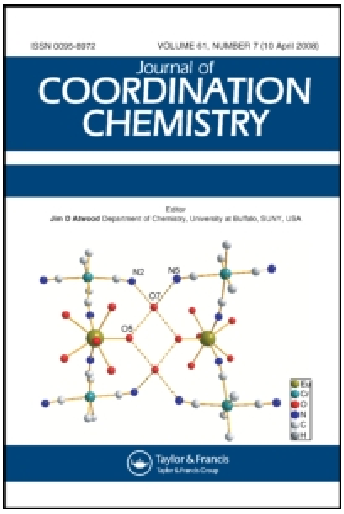

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Two tetrakis(benzoylacetonato)lanthanide species: synthesis, characterization and structures of tetrakis(benzoylacetonato)cerium(IV) and triethylammonium tetrakis(benzoylacetonato)lanthanate(III) tetrahydrate

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Tetrakis(benzoylacetonato)cerium(IV), [Ce(bzac)$_4$] and triethylammonium tetrakis (benzoylacetonato)lanthanate(III) tetrahydrate, [Et$_3$NH][La(bzac)$_4$]$\cdot$4H$_2$O were prepared and characterized by TG and DCS measurements, IR spectroscopy, and X-ray structure analysis. The coordination polyhedron of cerium is a trigonal dodecahedron, while that of lanthanum is a distorted square antiprism. Thermal and spectroscopic measurements indicate that bonding of the ligand to metal is stronger in [Ce(bzac)$_4$] than in [La(bzac)$_4$]$^-$.

Keywords: Lanthanide; β-Diketonate; Crystal structure; Octacoordination

1. Introduction

Tetrakis(β-diketonato) coordination compounds of rare earth metals can be divided into two groups, neutral species containing tetravalent metals and monoanions of trivalent metals; both have been widely studied. Neutral tetrachelates of cerium, uranium, thorium, and plutonium have long been investigated due to their volatility and possible use in lanthanide and actinide separation. Since compounds containing the same diketonate are usually isostructural, cerium compounds can be studied as good model compounds for their radioactive uranium, thorium, and plutonium analogues [1]. Tetrakis(β-diketonato)cerium(IV) compounds have also been studied as precursors for the growth of CeO$_2$ by metal organic chemical vapor deposition (MOCVD) and atomic layer epitaxy (ALE) [2]. The crystal structures for a range of tetrakis (β-diketonato)cerium(IV) compounds have been determined where β-diketone is acetylacetone [3], 2,2,6,6-tetramethylheptane-3,5-dione, 1-phenyl-5-methylhexane-1, 3-dione [4], dibenzoylmethane [1d, 5], 6,6,6-trifluoro-2,2-dimethyl-3,5-hexanedione [6], 2,2,7-trimethyl-3,5-octanedione [7], 2,6,6-trimethyl-2-methoxyheptane-3,5-dione [8], and hexafluoroacetylacetone [9].

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Anionic tetrakis(β-diketonato) lanthanide complexes have received attention due to their luminescent properties which enabled their use in flat-panel displays, luminescent probes in bioassays, laser materials, and UV-sensors [10] and also from the viewpoint of chiral catalysis [11] and molecular magnetism [12]. Although numerous crystal structures of tetrakis(β-diketonato)lanthanide(III) compounds have been reported, only a few tetrakis(β-diketonato)lanthanates(III) have been structurally characterized – compounds of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butadione [13], hexafluoroacetylacetone [1a] and heptafluorobutyryl-(+)-camphor [14].

A majority of studies have focused on acetylacetonato complexes with fluorinated diketonates due to their higher volatility; dibenzoylmethane and other symmetrical diketones have also been studied. Of compounds with asymmetrical diketones, most widely studied are those of thenoyltrifluoroacetone due to its effect on luminescent properties of the resulting compounds. Coordination of organic ‘‘antenna’’ ligands to lanthanide(III) can stimulate the forbidden 4f–4f transition [15].

Structural studies of complexes of benzoylacetone (Hbzac) are quite scarce. To the best of our knowledge, the only example of a tetrakis(benzoylacetonato) coordination complex that has been structurally characterized is tetrakis(benzoylacetonato) europate(III) $[Eu(bzac)_4]^-$, which was the anion in several salts [16]. In this article we report synthesis, thermal and spectroscopic characterization as well as molecular and crystal structures of two tetrakis(benzoylacetonato) species, tetrakis(benzoylacetonato) cerium(IV), $[Ce(bzac)_4]$ (**1**) and tetrakis(benzoylacetonato)lanthanate(III), $[La(bzac)_4]^-$, which were prepared as part of our ongoing investigation into the structures of transition metal benzoylacetonates. The latter was obtained as a salt of triethylammonium (**2**).

2. Experimental

2.1. *Synthesis of 1*

Cerium(III) chloride heptahydrate (3.72 g, 10 mmol) was dissolved in ethanol (20 mL) with heating and a solution of benzoylacetone (7.29 g, 45 mmol) in hot ethanol (15 mL) was added. To the resulting colorless solution, triethylamine (2 mL) was added and the color of the solution became dark red. Water (10 mL) was added and the mixture was left to cool at room temperature and then refrigerated. After 5 h, dark red, almost black crystals of compound **1** (6.58 g) were obtained.

2.2. *Synthesis of 2*

Lanthanum(III) nitrate hexahydrate (4.33 g, 10 mmol) was dissolved in ethanol : water mixture (1 : 1, 20 mL) with heating and a solution of benzoylacetone (7.29 g, 45 mmol) in hot ethanol (15 mL) was added. Triethylamine (7 mL) was added, and the resulting clear solution was diluted with water until it became cloudy. Then it was reheated to boiling, left to cool to room temperature, and then refrigerated overnight. After approximately 10 h, thin colorless needles of compound **2** (8.51 g) were obtained.

Table 1. Crystal data and summary of experimental details for **1** and **2**.

	1	**2**
Molecular formula	$C_{40}H_{36}O_8Ce$	$[C_6H_{16}N][C_{40}H_{36}O_8La]\ 4H_2O$
Formula weight	784.81	957.86
Crystal system	Tetragonal	Monoclinic
Space group	$I4_1/a$	$P2_1/n$
Unit cell dimensions (Å, °)		
a	16.4826(7)	15.9369(7)
b	16.4826(7)	19.3667(8)
c	12.6674(4)	16.1424(6)
α	90	90
β	90	102.636(4)
γ	90	90
V (Å^3)	3441.4(2)	4861.6(4)
Z	4	4
ρ_{Calcd} (g cm^{-3})	1.515	1.309
λ(Mo-Kα) (Å), graphite monochromator	0.71073	0.71073
T (K)	295(2)	295(2)
Crystal dimension (mm^3)	$0.11 \times 0.09 \times 0.08$	$0.26 \times 0.12 \times 0.06$
μ (mm^{-1})	1.376	0.936
$F(000)$	1592	1984
θ range (°)	3.66–27.00	3.75–27.00
Number of measured reflections	13,843	38,873
Number of independent reflections	1874	10,498
Number of reflections with $I > 2\sigma(I)$	1479	4907
Number of parameters	111	548
$R[F^2 > 4\sigma(F^2)]^a$	0.0380	0.0463
$wR(F^2)^b$	0.0857	0.0979
Goodness-of-fit, S^c	0.940	0.832

$^aR_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$.
$^bwR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$.
$^cS = \Sigma[w(F_o^2 - F_c^2)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

2.3. *X-ray structure determination*

The crystal and molecular structures of **1** and **2** were determined by single crystal X-ray diffraction. The diffraction data were collected at room temperature for both crystals. Diffraction measurements were made on an Oxford Diffraction Xcalibur Kappa CCD X-ray diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation [17]. The data sets were collected using the ω scan mode over the 2θ range up to 54°. The structures were solved by direct methods and refined using SHELXS and SHELXL [18, 19]. The structural refinement was performed on F^2 using all data. The hydrogen atoms were placed in calculated positions and treated as riding on their parent atoms, except hydrogens of water in **2** which could not be located. All calculations were performed and the drawings were prepared using WINGX crystallographic suite of programs [20]. The crystal data are listed in table 1.

2.4. *Thermal and spectroscopic analysis*

Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851 and DSC823 Modules in sealed aluminium pans (40 µL), heated in flowing nitrogen (200 mL min^{-1}) at 7°C min^{-1}. The TGA-measurements were performed between 25 and 625°C and the DSC measurements in the range between 25 and 500°C for both compounds.

Data collection and analysis were performed by the program package *STAR^e Software 9.01* [21].

Infrared spectra were recorded on an EQUINOX 55 FTIR spectrophotometer using KBr pellets. Data collection and analysis were performed by the program package *OPUS 4.0* [22]. ^{1}H NMR spectra were recorded on a Bruker Avance DPX300 spectrometer (300.13 MHz for ^{1}H) in $CDCl_3$. Chemical shifts are given in parts per million (ppm) relative to TMS.

3. Results and discussion

Both compounds were obtained in relatively high yields (84 and 89% for **1** and **2**, respectively). $[Et_3NH][La(bzac)_4] \cdot 4H_2O$ is poorly soluble in water and $[Ce(bzac)_4]$ is completely insoluble in water. Both compounds are soluble in somewhat polar organic solvents such as ethanol, acetone, and chloroform. Since the reaction took place in air, cerium was most likely oxidized by atmospheric oxygen.

$[Ce(bzac)_4]$ crystallizes in the space group $I4_1/a$ with the cerium positioned on the $\bar{4}$ axis, so that all the four rings are related by symmetry (figure 1). The cerium is coordinated by eight oxygens forming a distorted trigonal dodecahedron (figure 2). In two cerium(IV) diketonates closely related to **1**, tetrakis(dibenzoylmethanato)cerium(IV) [5] and tetrakis(1-phenyl-5-methylhexane-1,3-dionato)cerium(IV) [4] the coordination polyhedron is a distorted square antiprism. The Ce–O1 (acetyl) distance is somewhat longer (2.346 Å) than the Ce–O2 (benzoyl) distance (2.324 Å). Average Ce–O distances in **1** are shorter than in tetrakis(dibenzoylmethanato)cerium(IV) [5] and

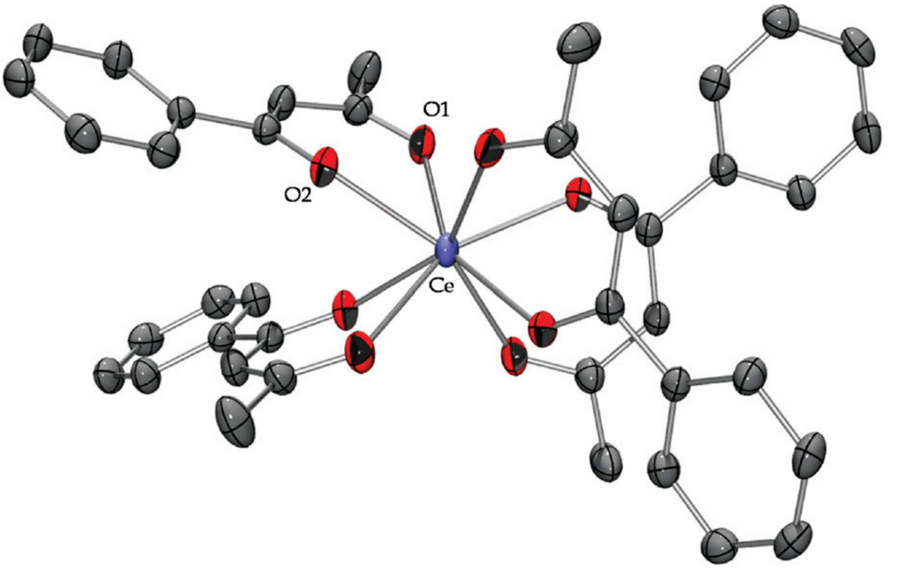

Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at 30% probability level and the hydrogens have been omitted for clarity.

comparable to the Ce–O bond lengths in tetrakis(acetylacetonato)cerium(IV) [3] and tetrakis(1-phenyl-5-methylhexane-1,3-dionato)cerium(IV) [4]. The bite distance is 2.72 Å. The chelate rings significantly deviate from planarity with the Ce atom displaced (0.725 Å) from the mean plane of the chelate ring (O1–C2–C3–C4–O2). This value is greater than usually noticed in tetrakis(β-diketonato)cerium(IV) compounds, but comparable to those encountered in tetrakis(dibenzoylmethanato) [1d, 5] (0.765 Å) and tetrakis(1-phenyl-5-methylhexane-1,3-dionato) [4] (0.762 Å) compounds, indicating steric hindrance of phenyl groups as its main cause. The ligand molecules themselves are not perfectly planar with the dihedral angle between the planes of chelate ring and the phenyl group of 9.69°.

The structure comprises discrete molecules with the strongest interaction of a C–H$\cdots\pi$ contact of 3.757 Å. Each phenyl group is both a hydrogen donor and an acceptor linking each molecule with four equivalent contacts to its neighbors along the *c*-axis.

$[Et_3NH][La(bzac)_4]\cdot 4H_2O$ crystallizes in the space group $P2_1/n$ with all the molecules in general positions (figure 3). The coordination polyhedron around lanthanum is a distorted square antiprism (figure 4) with bidentate ligands spanning opposite sides of each square face. The bite distances vary from 2.79 to 2.82 Å. The chelate rings in $[La(bzac)_4]^-$ deviate from planarity even more than in $[Ce(bzac)_4]$ with La displacements from the mean ring planes of the chelate rings ranging from 0.710 to 0.960 Å, comparable to those observed in tetrakis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butadionato) lanthanate(III) [13]. The ligands also deviate more from planarity than in $[Ce(bzac)_4]$ with the dihedral angles between the planes of chelate ring and the phenyl group in the range between 17.39° and 26.50°. The La–O bond lengths vary significantly from 2.452(4) to 2.532(3) Å, but are in general longer than the Ce–O bonds in **1** (average 2.491 Å in **2** and 2.345 Å in **1**). This is not unexpected, since the effective ionic radius of

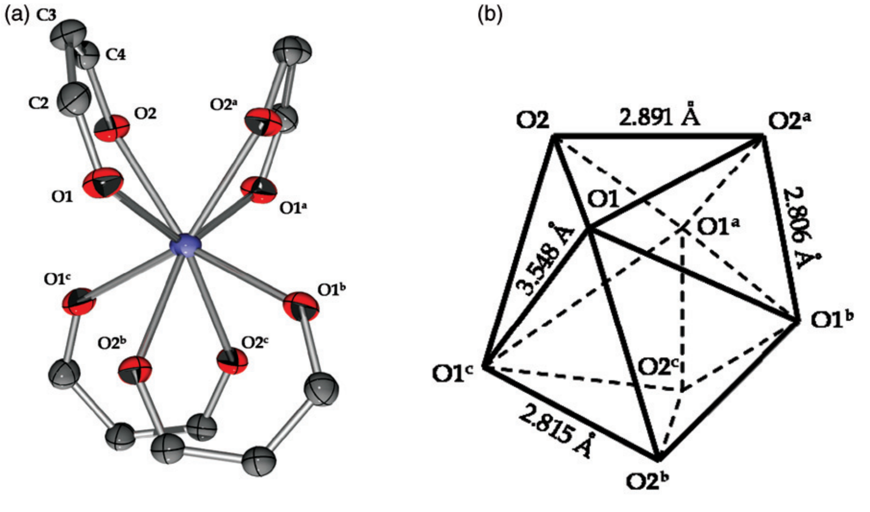

Figure 2. (a) Illustration of the coordination sphere around the cerium in **1** viewed perpendicular to the $\bar{4}$ axis of the CeO_8 dodecahedron. (b) Schematic representation of the coordination sphere with the symmetrically independent non-bonding interatomic distances.

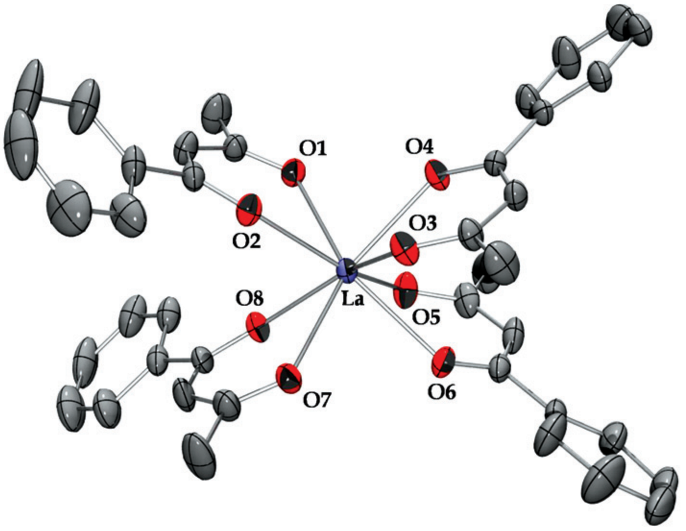

Figure 3. Molecular structure of the anion of **2**. Thermal ellipsoids are shown at 30% probability level and the hydrogens have been omitted for clarity.

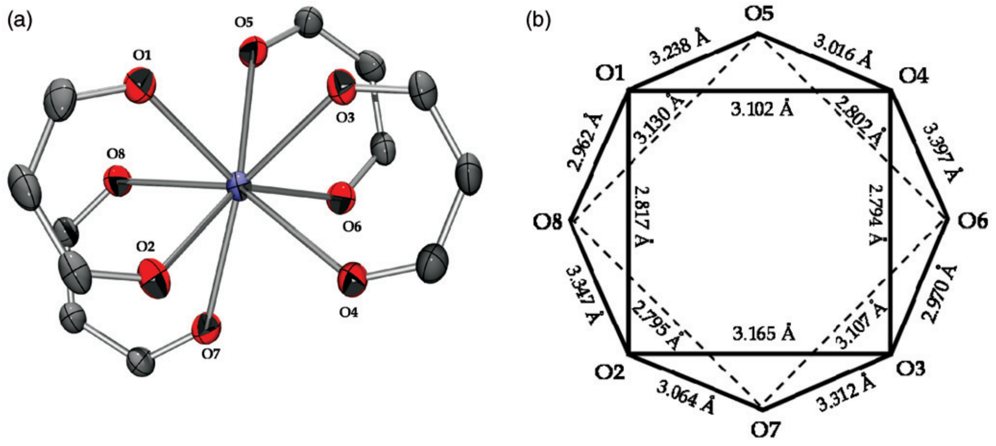

Figure 4. (a) The coordination sphere around the lanthanum in **2** viewed along the approximate $\bar{8}$ axis of the LaO_8 antiprism. (b) Schematic representation of the coordination sphere with the non-bonding interatomic distances.

lanthanum(III) is larger (1.16 Å) than the effective ionic radius of cerium(IV) (0.97 Å) in octacoordinated species [23].

In all chelate rings but one, the La–O(acetyl) distances are noticeably longer than the La–O(benzoyl) distances. The differences in bond lengths are greater than those in the cerium compound, attributed to hydrogen bonding in which acetyl oxygens participate (figure 5), whereas the benzoyl oxygens do not, most likely due to the steric hindrance of the phenyl ring.

As noted earlier, the only [M(bzac)$_4$] species reported to date is [Eu(bzac)$_4$]$^-$. In [Eu(bzac)$_4$]$^-$, the coordination polyhedron around the europium atom is also a distorted

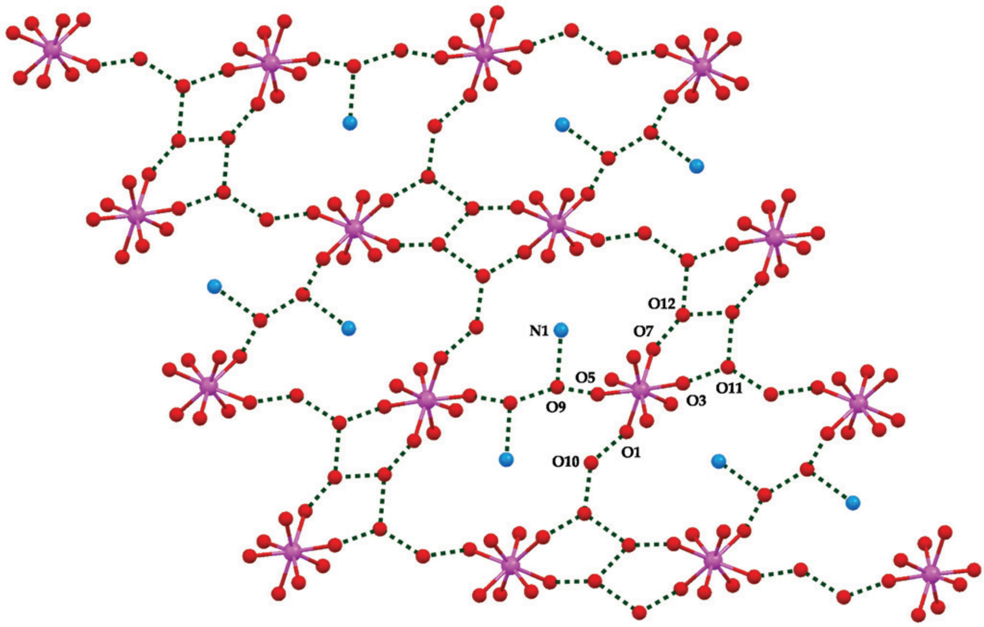

Figure 5. The hydrogen bonding array in **2** in the (1 0 $\bar{1}$) plane. Hydrogen and carbon atoms have been omitted for clarity.

antiprism with the bidentate ligands spanning opposite sides of each square face as for lanthanum in $[La(bzac)_4]^-$. However, the relative orientations of the benzoylacetonato ligands greatly differ in these species. Unlike in $[Eu(bzac)_4]^-$ where all the ligands are oriented in the same direction (approximate symmetry of the ion is C_2), in $[La(bzac)_4]^-$ the orientation of the ligands alternates (approximate symmetry of the ion is D_2). It is therefore obvious that the central lanthanide atom influences the ligand orientation, thus greatly changing the geometry of the entire coordination species.

The crystal structure consists of hydrogen bonded layers of molecules perpendicular to the [1 0 $\bar{1}$] direction (figure 5). All the water molecules, the triethylammonium nitrogen, and all four acetyl oxygens of each complex anion participate in hydrogen bonding. All these atoms are placed about the (1 0 $\bar{1}$) plane with the largest displacement of 1.103 Å for O5. The hydrophobic hydrocarbon segments of both the cations and anions belonging to the molecules of the neighboring layers occupy the space between the (1 0 $\bar{1}$) planes. There are no significant short contacts between molecules belonging to the neighboring layers with the shortest intermolecular contact C18–H $\cdots$ C49 (C–H $\cdots$ π) of 3.825 Å. Hydrogen bonding of the water molecules probably causes the H_2O protons to be disordered, and thus makes locating the H_2O protons in the structure impossible.

The IR spectra of both compounds contain several bands characteristic for β-diketonate metal coordination compounds. The C–O stretching bands appear at 1551 and 1518 cm^{-1} for $[Ce(bzac)_4]$ and at 1564 and 1522 cm^{-1} for $[Et_3NH][La(bzac)_4] \cdot 4H_2O$. The IR spectrum of the free ligand shows one band at 1610 cm^{-1}. Larger shift of the carbonyl stretching frequency in **1** as opposed to **2** suggests a larger transfer of electron density from the carbonyl groups to the Ce–O bonds than to La–O bonds, i.e., that the Ce–O bonds are stronger than the La–O bonds. In the spectrum of **2** there is also a broad peak between 3100 and 3500 cm^{-1} corresponding to the O–H and N–H stretching indicative of the hydrogen bonding of water and triethylammonium (table 2).

In the ^1H NMR spectra of both compounds only one set of signals for the protons of the benzoylacetonate ligands is present. The chemical shifts of all the protons in $[Ce(bzac)_4]$ (1.143 ppm (CH_3), 3.108 ppm (CH), and C_6H_5 multiplet at 7.282 ppm) are shifted upfield compared to $[La(bzac)_4]^-$ (1.010 ppm (CH_3), 2.514 ppm (CH), and C_6H_5 multiplet at 7.244 ppm). The difference in the chemical shifts is most pronounced for the chelate proton ($\Delta = 0.594$ ppm) and the least for the phenyl multiplet ($\Delta = 0.038$ ppm).

The DSC curve of $[Ce(bzac)_4]$ shows one endothermic peak at 188°C (54.0 $kJ\,mol^{-1}$), which corresponds to the compound's melting point. The compound is stable until the pyrolitic decomposition which starts taking place at 294°C and continues over the entire temperature range. The final residue weighs 22.3% of the original mass and corresponds to CeO_2 (Calcd 21.9%). Thermal analysis of $[Et_3NH][La(bzac)_4] \cdot 4H_2O$ has shown it to be surprizingly unstable. The first drop in mass of 2.8% occurs already at 41°C with the corresponding reaction enthalpy of 100.2 $kJ\,mol^{-1}$. The mass of the resulting compound is then stable up to 95°C when a continuous reduction of mass begins to take place and continues over the entire temperature range. A wide exothermic peak in the DSC curve with an onset of 264°C ($-68.24\,kJ\,mol^{-1}$) most probably marks the beginning of the decomposition of the $[La(bzac)_4]^-$ anion. The final residue weighs 17.0% of the original mass and corresponds to La_2O_3 (Calcd 16.9%).

Thermal analysis of $[Ce(bzac)_4]$ indicates that it does not sublime, at least at atmospheric pressure, as some other cerium(IV) diketonates do, and would thus be unsuitable as a CVD precursor for preparation of ceria. This can most likely be attributed to the $C–H \cdots \pi$ interactions in the structure. Although the $C–H \cdots \pi$ contacts are quite long, the overall effect of eight such contacts in which each molecule participates is probably sufficiently strong to prevent sublimation, at least until the temperature becomes sufficient to cause decomposition of the molecule itself. Similar behavior was noted in tetrakis(1-phenyl-5-methylhexane-1,3-dionato)cerium(IV) [4] where the structure is also stabilized by weak hydrogen bonding with phenyl rings as hydrogen acceptors.

It is somewhat difficult to account for the thermal instability of $[Et_3NH][La(bzac)_4] \cdot 4H_2O$. The initial loss of mass of 2.8% could be attributed to loss of approximately 26% of triethylamine or 37% of water. Either explanation is not entirely satisfactory since the temperature on which the change occurs (41°C) is quite lower than the boiling points of both triethylamine (89.7°C) and water (100°C). We believe the most probable explanation is that the change is in fact decomposition of the tetrahydrate upon which a part of the released water evaporated due to the local overheating induced by the rather large exothermicity of the process. The continuous loss of mass from 95°C onwards corresponds probably to the evaporation of remaining water, later loss of triethylamine and, finally, decomposition of the ligands. Taking into account the hydrogen bonding array in the structure of $[Et_3NH][La(bzac)_4] \cdot 4H_2O$, it is somewhat surprizing that it should be such an unstable substance, although such cases are not unprecedented. For instance, extreme instability of highly hydrogen bonded tetrakis(acetylacetonato)cerium(IV) decahydrate has been reported [24]. Its crystal structure consists of hydrogen bonded layers of water molecules placed between the layers of hydrophobic chelate molecules and is thus similar to the layered structure

Table 2. Geometric parameters of lanthanide coordination spheres in **1** and **2**.

1	
d (Å)	
Ce–O1	2.346(2)
Ce–O2	2.324(2)
Angle (°)	
O1–Ce–O2	71.28(8)
O1–Ce–O2[a]	74.14(9)
O1–Ce–O2[b]	73.87(8)
O1–Ce–O2[c]	150.70(8)
O1–Ce–O1[a]	135.40(11)
O1–Ce–O1[b]	98.28(4)
O2–Ce–O2[a]	76.92(11)
O2–Ce–O2[b]	127.82(7)
2	
d (Å)	
La–O1	2.527(3)
La–O2	2.452(4)
La–O3	2.532(3)
La–O4	2.463(3)
La–O5	2.491(3)
La–O6	2.492(4)
La–O7	2.499(3)
La–O8	2.474(3)
Angle (°)	
O1–La–O2	68.84(11)
O1–La–O3	124.14(11)
O1–La–O4	77.01(12)
O1–La–O5	80.50(12)
O1–La–O6	147.77(12)
O1–La–O7	128.80(12)
O1–La–O8	72.56(11)
O2–La–O3	78.90(12)
O2–La–O4	104.10(12)
O2–La–O5	148.44(12)
O2–La–O6	142.95(12)
O2–La–O7	76.32(12)
O2–La–O8	85.51(12)
O3–La–O4	68.08(11)
O3–La–O5	126.86(13)
O3–La–O6	72.40(12)
O3–La–O7	82.25(11)
O3–La–O8	149.28(11)
O4–La–O5	75.02(12)
O4–La–O6	86.56(13)
O4–La–O7	149.37(12)
O4–La–O8	142.11(11)
O5–La–O6	68.44(13)
O5–La–O7	120.66(13)
O5–La–O8	78.14(12)
O6–La–O7	77.04(13)
O6–La–O8	107.80(12)
O7–La–O8	68.33(11)

in $[Et_3NH][La(bzac)_4] \cdot 4H_2O$. The probable start of the thermal decomposition of the lanthanum complex is identified at 264°C, 30°C lower than that of the cerium complex. This is in accord with the weaker bonding of benzoylacetonate to lanthanum(III) than to cerium(IV), as proposed based on IR spectra. Larger charge of the cerium ion as well as its smaller ionic radius enables stronger bonding of benzoylacetonate to cerium(IV).

4. Conclusion

The reaction of $CeCl_3$ with benzoylacetone in alkaline medium under air yielded a neutral species $[Ce(bzac)_4]$, while $La(NO_3)_3$ under same conditions yields a salt containing $[La(bzac)_4]^-$. The coordination polyhedron in $[Ce(bzac)_4]$ is a trigonal dodecahedron while in $[La(bzac)_4]^-$ it is a distorted square antiprism. Spectroscopic and thermal studies indicate stronger bonding of benzoylacetonato to cerium(IV) than to lanthanum(III). The results presented in this article, together with the literature data on $[Eu(bzac)_4]^-$, indicate a significant influence of the lanthanide ion on the geometry of $[Ln(bzac)_4]$ species. A further structural study of tetrakis(benzoylacetonato)lanthanide species could yield interesting results both from the stereochemical point of view and subsequently for the possible use of such complexes in lanthanide separation.

Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk). These data can be obtained free of charge from the Director upon request quoting the CCDC deposition number CCDC 703714 and CCDC 703715.

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