Inorganica Chimica Acta, 193 (1992) 9–15

Synthesis and crystal structures of the dinuclear complexes [{LM(acac)$_2$}$_2$O](ClO$_4$)$_2$ (M = Zr(IV), Hf(IV); L = 1,4,7-triazacyclononane) containing μ-oxo bridged eight-coordinate metal(IV) ions

Peter Jeske, Karl Wieghardt*
Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-4630 Bochum (FRG)

Bernhard Nuber and Johannes Weiss
Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg (FRG)

(Received September 10, 1991)

Abstract

The monomeric tetrakis(2,4-pentanedionato) complexes of zirconium(IV) and hafnium(IV) have been shown to react in acetone/water (95:5) mixtures with 1,4,7-triazacyclononane (L) affording upon addition of NaClO$_4$ colorless crystals of [{LZr(acac)$_2$}$_2$O](ClO$_4$)$_2$ and [{LHf(acac)$_2$}$_2$O](ClO$_4$)$_2$, respectively. Crystal data for the zirconium species (and in brackets for the corresponding hafnium complex): monoclinic space group: $P2_1/n$ ($P2_1/n$), a = 10.731(3) (10.701(5)), b = 36.60(1) (36.58(1)), c = 11.562(3) (11.552(3)) Å, β = 96.13(2)° (96.16(3)°). Each metal(IV) ion is coordinated to two didentate 2,4-pentanedionato ligands and a tridentate macrocyclic amine. Two such units are linked by a bent μ-oxo bridge (Zr(1)–O–Zr(2) 150.4(2)°; Hf(1)–O1–Hf(2) 151.3(3)°) which completes the eight-coordination at each metal centre. The M–O$_{oxo}$ bonds are quite short (Zr–O$_{oxo}$ 1.961(4), 1.975(4) Å; Hf–O$_{oxo}$ 1.950(6), 1.976(6) Å).

Introduction

The structural chemistry of μ-oxo bridged organometallic dinuclear complexes of zirconium(IV) [1] and hafnium(IV) is reasonably well established and a number of X-ray structures of such species have been published, e.g. (Cp$_2$HfMe)$_2$O [2], (Cp$_2$ZrCl)$_2$O [3], (Cp$_2$ZrMe)$_2$O [4], [{(Me$_2$Si)$_2$N}$_2$ZrMe]$_2$O [5], [CpZr(SPh)]$_2$O [6]. In contrast, the M–O–M unit has not been structurally characterized in classical Werner-type coordination compounds with nitrogen/oxygen donor ligands although such species have often been encountered as hydrolysis reaction products of mononuclear zirconium(IV) and hafnium(IV) complexes [7].

Here we report the synthesis and crystal structures of two such compounds [{LM^{IV}(acac)$_2$}$_2$O](ClO$_4$)$_2$ where L represents the tridentate macrocycle 1,4,7-triazacyclononane, acac is 2,4-pentanedionate(1−), and M(IV) is Zr(IV) and Hf(IV).

Experimental

1,4,7-Triazacyclononane [8] and Hf(acac)$_4$ [9] were prepared as described in the literature. All other reagents and solvents used were obtained from commercial sources.

Synthesis of [{LZr(acac)$_2$}$_2$O](ClO$_4$)$_2$ (1)

To a suspension of Zr(acac)$_4$ (5.0 g; 10.25 mmol) in acetone (20 ml) which contained ≈5% water was added the ligand 1,4,7-triazacyclononane (2.0 g; 15.5 mmol) and NaClO$_4$ (2.0 g). After heating under reflux for 5 h, a clear yellowish solution was obtained from which a microcrystalline colorless precipitate formed upon cooling to 10 °C. The crystals were collected by filtration, washed with diethyl ether and air-dried (yield: 4.8 g, 89%). Slow recrystallization of this material from an acetonitrile solution produced translucent colorless prismatic crystals suitable for an X-ray structure determination. *Anal.* Calc. for $C_{32}H_{58}Cl_2O_{17}N_6Zr_2$: C, 36.53; H, 5.56; N, 7.99; ClO$_4$, 18.90. Found: C, 36.3; H, 5.6; N, 7.8; ClO$_4$, 18.9%. IR (KBr disk, cm^{-1}): ν(Zr–O–Zr): 710. ^{1}H NMR (80 MHz; CD$_3$CN; δ, ppm): 5.7 (s, 2H); 5.6 (s, 2H); 4.2 (broad signal, 6H, amine protons); 3.4

---

*Author to whom correspondence should be addressed.

0020-1693/92/$5.00

(m, 12H; -CH_2-); 2.8 (m, 12H; -CH_2-); 2.05 (s, 6H); 1.95 (s, 12H); 1.85 (6H).

Synthesis of [{LHf(acac)$_2$}$_2$O](ClO_4)$_2$ (2)

The preparation of **2** was completely analogous to the synthesis of **1**. Hf(acac)$_4$ [9] was used as starting material (10.0 mmol). The microcrystalline colorless precipitate was recrystallized from a CH_3CN solution which gave translucent prismatic crystals suitable for an X-ray structure determination (yield ≈ 90%). *Anal.* Calc. for $C_{32}H_{58}Cl_2O_{17}N_6Hf_2$: C, 31.3; H, 4.7; N, 6.85; ClO_4, 16.2. Found: C, 31.1; H, 4.5; N, 6.7; ClO_4, 16.25% IR (KBr disk; cm^{-1}): ν(Hf–O–Hf): 740. ^1H NMR (80 MHz; CD_3CN; δ, ppm): 5.65 (s, 2H); 5.55 (s, 2H); 4.1 (broad signal, 6H; amine protons); 3.4 (m, 12H); 2.8 (m, 12H); 2.05 (s, 6H).

X-ray structure determinations

Crystallographic parameters, details of intensity measurements and of structure refinements are summarized in Table 1. The unit cell parameters of **1** and **2** are based on 28 reflections with $3.5 < 2\theta < 27°$, respectively. Calculations were performed on a Micro VAX II computer by using the SHELXTL-PLUS [10] program package. Crystals of **1** and **2** were found to belong to the monoclinic space group $P2_1/n$ (No 14). Lorentz and polarization corrections were applied in the usual manner, empirical absorption corrections using ψ-scans of 9 reflections ($3.7 < 2\theta < 56°$), respectively, were also applied; no correction for extinction was attempted. The structures were solved by the use of the Patterson heavy-atom method and subsequent difference Fourier syntheses. The structures were refined by the full-matrix least-squares methods, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ ($w = 1/\sigma^2(F_o)$). All non-hydrogen atoms were refined with anisotropic thermal parameters; corrections for anomalous scattering were applied to these atoms [11]. Hydrogen atoms were included in calculated positions in the final refinement cycles. Final atom parameters are listed in Table 2 for **1** and Table 3 for **2**.

Results and discussion

Reaction of the mononuclear tetrakis(acetylacetonato)metal(IV) complexes (Zr(IV), Hf(IV)) in water-containing acetone with the tridentate macrocycle 1,4,7-triazacyclononane (L) affords a clear, yellowish solution from which upon addition of $NaClO_4$, colorless crystals of [{LM^{IV}(acac)$_2$}$_2$O](ClO_4)$_2$ are obtained in *c.* 90% yield. Thus two didentate acac$^-$ ligands are replaced by a tridentate amine leaving one coordination site of the former eight coordinate M(acac)$_4$ species

TABLE 1. Crystallographic data for **1** and **2**

	1	**2**
Formula	$C_{32}H_{58}O_9N_6Zr_2(ClO_4)_2$	$C_{32}H_{58}N_6O_9Hf_2(ClO_4)_2$
Formula weight	1052.18	1226.7
Color	colorless	colorless
Space group	$P2_1/n$	$P2_1/n$
a (Å)	10.731(3)	10.701(5)
b (Å)	36.60(1)	36.58(1)
c (Å)	11.562(3)	11.552(3)
β (°)	96.13(2)	96.16(3)
V (Å^3)	4515.06	4496.1
Z	4	4
T (°C)	22(1)	22(1)
Radiation	Mo Kα	Mo Kα
ρ_{calc} (g cm^{-3})	1.55	1.81
Crystal dimensions (mm)	0.80 × 0.80 × 0.80	0.15 × 0.25 × 0.80
μ(Mo Kα) (mm^{-1})	0.64	4.76
Transmission coefficient (min.–max.)	0.39–0.757	0.447–0.941
Scan type	ω	ω
Octant	$+h, +k, \pm l$	$+h, +k, \pm l$
2θ-range (°)	$2 < 2\theta < 55$	$3 < 2\theta < 55$
No. reflections	11055	10944
No. unique data $I > 2.5\sigma(I)$	6351	6812
No. parameters	533	533
$R(F_o)$	0.062	0.053
$R_w(F_o^2)$	0.051	0.042
GOF	2.50	1.98
Diffractometer	Syntex R3	Syntex R3
Max. resid. electr. density (e/Å^3)	0.67 (−0.55)	1.08 (−0.96)

TABLE 2. Atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$) for **1**

Atom	x/a	y/b	z/c	U_{eq}
Zr(1)	1733(1)	1654(1)	4734(1)	39(1)
Zr(2)	2560(1)	945(1)	2533(1)	37(1)
O(1)	2047(3)	1392(1)	3315(3)	39(1)
O(2)	613(4)	1730(1)	6237(4)	55(2)
O(3)	−150(4)	1775(1)	3950(4)	56(2)
C(7)	−878(7)	1681(2)	7592(6)	81(3)
C(8)	−553(7)	1717(2)	6365(6)	54(3)
C(9)	−1480(6)	1726(2)	5441(6)	60(3)
C(10)	−1257(7)	1766(2)	4302(7)	58(3)
C(11)	−2332(6)	1808(2)	3376(6)	80(3)
O(4)	712(4)	1129(1)	4971(3)	44(1)
O(5)	2930(4)	1376(1)	6026(3)	49(2)
C(12)	−229(7)	612(2)	5709(6)	69(3)
C(13)	802(6)	894(2)	5781(5)	47(2)
C(14)	1775(7)	883(2)	6682(5)	55(3)
C(15)	2783(7)	1113(2)	6757(5)	53(3)
C(16)	3856(6)	1077(2)	7715(5)	74(3)
N(1)	2431(5)	2189(2)	5927(5)	60(2)
N(2)	1725(6)	2214(1)	3584(5)	61(2)
N(3)	3876(5)	1843(1)	4434(5)	54(2)
C(1)	1716(10)	2504(2)	5447(7)	116(5)
C(2)	1499(10)	2529(2)	4261(8)	104(5)
C(3)	2844(9)	2243(3)	2974(8)	120(5)
C(4)	3938(8)	2058(2)	3393(8)	93(4)
C(5)	4553(7)	2013(2)	5489(7)	86(4)
C(6)	3775(8)	2249(3)	6109(8)	109(5)
O(6)	4025(4)	533(1)	2141(3)	52(2)
O(7)	3793(4)	1243(1)	1527(3)	53(2)
C(27)	5768(7)	198(2)	1676(6)	72(3)
C(28)	5056(6)	549(2)	1709(5)	53(3)
C(29)	5521(7)	866(2)	1261(6)	63(3)
C(30)	4892(7)	1194(2)	1191(5)	54(3)
C(31)	5431(7)	1519(2)	636(5)	71(3)
O(8)	2401(4)	545(1)	3837(3)	42(1)
O(9)	4265(4)	1048(1)	3823(3)	45(2)
C(32)	6081(6)	984(2)	5160(6)	72(3)
C(33)	4834(6)	848(2)	4609(5)	46(2)
C(34)	4352(6)	516(2)	4981(5)	48(2)
C(35)	3181(6)	388(2)	4606(5)	44(2)
C(36)	2721(6)	36(2)	5072(6)	61(3)
N(4)	1347(5)	1212(1)	873(4)	49(2)
N(5)	285(5)	837(1)	2591(4)	46(2)
N(6)	1697(5)	457(1)	1202(4)	53(2)
C(21)	159(6)	1362(2)	1210(5)	56(3)
C(22)	−551(6)	1072(2)	1792(5)	59(3)
C(23)	−4(6)	446(2)	2414(5)	57(3)
C(24)	437(6)	319(2)	1297(6)	61(3)
C(25)	1861(7)	615(2)	29(5)	67(3)
C(26)	1144(7)	972(2)	−172(5)	66(3)
Cl(1)	2215(3)	2155(1)	9375(2)	81(1)
O(11)	1374(9)	2136(3)	10232(7)	199(5)
O(12)	1544(6)	2333(1)	8438(5)	119(3)
O(13)	3244(7)	2336(2)	9838(7)	171(4)
O(14)	2433(7)	1796(2)	9121(6)	140(4)
Cl(2)	7494(2)	581(1)	8510(2)	66(1)
O(21)	6736(10)	447(3)	7704(7)	270(7)
O(22)	7569(6)	369(2)	9503(5)	132(3)
O(23)	7212(10)	928(2)	8723(8)	217(6)
O(24)	8650(8)	585(3)	8125(7)	199(5)

TABLE 3. Atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$) for **2**

Atom	x/a	y/b	z/c	U_{eq}
Hf(1)	1737(1)	1654(1)	4726(1)	38(1)
Hf(2)	2559(1)	945(1)	2525(1)	36(1)
O(1)	2058(6)	1391(2)	3322(5)	37(2)
O(2)	633(7)	1729(2)	6241(6)	54(3)
O(3)	−150(7)	1769(2)	3952(6)	51(3)
C(7)	−881(11)	1680(3)	7575(10)	82(6)
C(8)	−535(12)	1714(3)	6364(11)	57(5)
C(9)	−1486(10)	1722(3)	5450(10)	54(4)
C(10)	−1245(11)	1758(3)	4309(11)	53(5)
C(11)	−2316(10)	1808(3)	3368(10)	70(5)
O(4)	709(6)	1132(2)	4965(6)	43(3)
O(5)	2921(6)	1381(2)	6007(6)	45(3)
C(12)	−239(11)	615(3)	5711(10)	68(5)
C(13)	787(11)	892(3)	5757(10)	46(4)
C(14)	1773(11)	886(3)	6682(10)	54(5)
C(15)	2809(11)	1125(3)	6749(9)	51(4)
C(16)	3874(11)	1085(3)	7710(9)	71(5)
N(1)	2409(9)	2179(2)	5945(8)	60(4)
N(2)	1721(9)	2204(2)	3567(8)	53(4)
N(3)	3878(8)	1830(2)	4433(8)	49(3)
C(1)	1693(16)	2504(3)	5425(13)	105(8)
C(2)	1500(15)	2528(3)	4224(12)	94(7)
C(3)	2815(15)	2234(5)	2983(12)	120(9)
C(4)	3910(13)	2052(3)	3389(12)	85(7)
C(5)	4547(11)	2010(3)	5502(11)	79(6)
C(6)	3761(13)	2245(4)	6105(12)	96(7)
O(6)	4011(7)	530(2)	2140(6)	49(3)
O(7)	3788(7)	1241(2)	1538(6)	50(3)
C(27)	5784(12)	197(3)	1667(10)	77(6)
C(28)	5042(11)	544(3)	1705(9)	51(4)
C(29)	5528(11)	859(3)	1259(10)	54(5)
C(30)	4904(12)	1189(3)	1199(9)	52(4)
C(31)	5451(11)	1513(3)	659(9)	69(5)
O(8)	2391(6)	550(2)	3818(5)	37(2)
O(9)	4267(6)	1045(2)	3795(6)	40(2)
C(32)	6078(10)	984(3)	5164(10)	66(5)
C(33)	4834(10)	853(3)	4597(9)	39(4)
C(34)	4346(10)	520(3)	4959(9)	44(4)
C(35)	3184(11)	395(3)	4586(9)	43(4)
C(36)	2706(10)	37(3)	5056(10)	61(5)
N(4)	1385(8)	1212(2)	867(7)	43(3)
N(5)	297(8)	846(2)	2596(7)	40(3)
N(6)	1740(9)	458(2)	1196(7)	51(3)
C(21)	170(11)	1357(3)	1198(10)	57(5)
C(22)	−557(10)	1069(3)	1798(9)	56(4)
C(23)	−1(10)	450(3)	2411(9)	57(5)
C(24)	439(11)	326(3)	1265(10)	59(5)
C(25)	1872(12)	615(3)	49(9)	64(5)
C(26)	1156(12)	972(3)	−159(9)	64(5)
Cl(1)	2221(4)	2158(1)	9368(3)	77(2)
O(11)	1371(15)	2139(4)	10204(12)	195(9)
O(12)	1549(11)	2329(2)	8418(9)	115(5)
O(13)	3242(12)	2343(3)	9818(12)	177(8)
O(14)	2424(11)	1799(3)	9115(10)	140(6)
Cl(2)	7500(4)	584(1)	8515(3)	63(1)
O(21)	6779(17)	444(4)	7675(12)	254(10)
O(22)	7554(11)	371(3)	9494(8)	133(6)
O(23)	7268(15)	937(3)	8722(13)	195(9)
O(24)	8640(15)	587(4)	8124(11)	200(9)

available for a unidentate ligand. This ligand is presumably a water molecule (or hydroxide) yielding $[LM(acac)_2OH_2]^{2+}$ or $[LM(acac)_2OH]^{+}$ intermediates which dimerize in the basic reaction conditions with formation of a μ-oxo bridge, eqn. (1):

$$2M(acac)_4 + H_2O + 2L \longrightarrow [L(acac)_2M\text{–}O\text{–}M(acac)_2L]^{2+} + 2acacH \qquad (1)$$

M = Zr, Hf

Recrystallization of the colorless perchlorate salts from acetonitrile solution yields colorless, translucent single crystals of $[\{L_2Zr(acac)_2\}_2O](ClO_4)_2$ (**1**) and $[\{L_2Hf(acac)_2\}_2O](ClO_4)_2$ (**2**). **1** and **2** are soluble in CH_3CN, acetone, CH_2Cl_2 and CH_3NO_2 but only sparingly in H_2O. Both species are stable in dilute acid solutions (HCl, $HClO_4$) and base (NaOH). Concentrated acids ($[H^+] > 1.0$ M) induce the dissociation of the amine ligands as was judged by the recovery of solid $[LH_3]X_3$ salts (X = Cl, ClO_4) from such solutions.

In the IR spectrum (KBr disks) the ν_{as}(M–O–M) stretching frequency is observed at 710(vs) cm^{-1} for **1** and 740(vs) cm^{-1} for **2**. For $[(\eta^5\text{-}C_5H_5)_2Hf(CH_3)]_2O$ this frequency has been observed as an intense, broad absorption between 760 and 790 cm^{-1} [2], and the same characteristic band has been reported for the trimer $[(\eta^5\text{-}C_5H_5)_2ZrO]_3$ [12]. Both **1** and **2** display two well resolved sharp ν(N–H) frequencies of equal intensity at 3298, 3248 and 3300, 3250 cm^{-1}, respectively.

The ^1H NMR spectra (80 MHz) of **1** and **2** measured in CD_3CN are very similar: the most interesting feature is the observation of two singlets at δ 5.70, 5.60 and δ 5.65, 5.55, respectively. Each resonance corresponds to two protons per dinuclear unit and is due to the tertiary protons of four coordinated $acac^-$ ligands. The two $acac^-$ ligands at each metal(IV) ion are magnetically inequivalent. A broad resonance at δ 4.2 for **1** and 4.1 for **2** is assigned to N–H protons of the coordinated amine. The intensity of this signal decreases upon addition of a few drops of D_2O. The methylene protons of the cyclic amine give rise to two complicated multiplets centered at δ 3.4 and 2.8 for both **1** and **2**. Interestingly, three singlets have been observed for the eight methyl groups per dinuclear unit two of which correspond each to 6 protons whereas the third resonance accounts for 12 protons. As will be shown below, the two halves of the $[\{LM(acac)_2\}_2O]^{2+}$ dications are identical. Therefore, we propose that the observed inequivalence of the methyl resonances is due to the inequivalence of the two coordinated $acac^-$ ligands at each metal ion. In the solid state structure it appears that the six-membered chelate $\overline{\text{M–O5–C15–C14–C13–O4}}$ is slightly more asymmetric than the corresponding $\overline{\text{M–O2–C8–C9–C10–O3}}$ ring. Consequently, the two CH_3 groups attached to C13 and C15 in **1** resonate at δ 2.05 and 1.85 whereas those bound to C8 and C10 give rise to only one signal at δ 1.95 (12H). For **2** these resonances are observed at δ 2.05 (6H), 1.80 (6H) and 1.85 (12H).

Figure 1 shows a perspective view of the dication in crystals of **1**. The structure of the corresponding cation in crystals of **2** is virtually identical (see 'Supplementary material'). The atom labeling scheme (Fig. 1) is identical for both structures **1** and **2**. Selected bond distances for **1** and (in parenthesis) **2** are summarized in Table 4. Selected bond angles of one half of the dications of **1** (and in parenthesis) of **2** are given in Table 5.

Crystals of **1** and **2** are isostructural and isomorphous. The packing of cations and anions are identical and, consequently, the atom coordinates $x/a, y/b, z/c$ are the same within experimental error for both structures.

The metal ions in structures **1** and **2** are all eight-coordinate; their ligand environment is composed of three amine nitrogen atoms, four oxygen atoms of two didentate acetylacetonato(1−) ligands and one μ_2-oxo bridge.

It is worth noting that corresponding metal–ligand distances and bond angles in **1** and **2** are identical within three times the e.s.d. (3σ). This is a common feature for Zr(IV) and Hf(IV) complexes containing the same set of ligands. The dications in **1** and **2** do not possess crystallographically imposed symmetry. It is therefore significant that the dimensions of the two coordination polyhedra of a dication are identical within the limits of 3σ.

The M–O–M unit is strongly bent in both structures (av. 150.8°). By comparison with μ-oxo bridge organometallic complexes compiled in Table 6 it is clear that **1** and **2** have the most strongly bent M–O–M unit (M = Zr(IV), Hf(IV)) observed up to now. The average $M\text{–}O_{oxo}$ distance at 1.965 Å is quite short and agrees well with those structures shown in Table 6. As has been discussed previously [2, 6] the short $M\text{–}O_{oxo}$ distance is attributed to bonding (d–p) π interactions between empty metal d-orbitals and filled p-orbitals of the oxo bridge.

Nevertheless it is somewhat counterintuitive that strong bending of the M–O–M group from 180 to 150.8° obviously does not lead to a significant increase of the $M\text{–}O_{oxo}$ bond length. Even in trimeric $[(\eta^5\text{-}C_5H_5)_2ZrO]_3$, which contains a six-membered $Zr_3(\mu\text{-}O)_3$ ring and Zr–O–Zr angles of 142.5° [12], the $Zr\text{–}O_{oxo}$ distance is quite short (1.959(3) Å).

The geometry of the coordination polyhedra around each metal ion may best be described as distorted dodecahedral as is shown schematically in Fig. 2 which is quite common for eight-coordinate complexes of Zr(IV) and Hf(IV). To our knowledge **1** and **2** represent the first structurally characterized species where two dodecahedra are connected by a μ-oxo bridge.

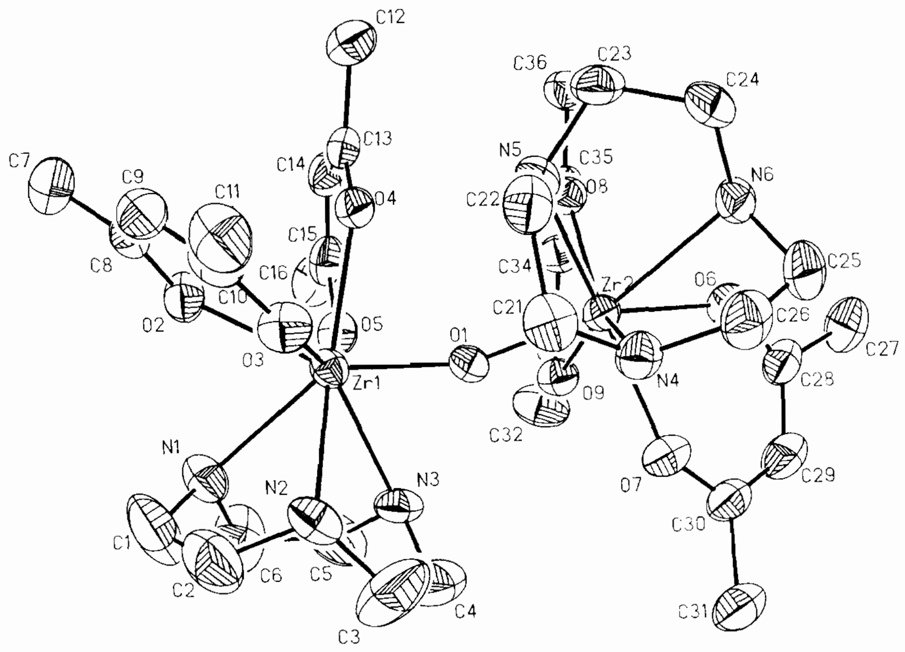


Fig. 1. Perspective view of the dication in crystals of **1**. The atom labeling scheme is the same for structures **1** and **2** (except Zr1 is Hf1 and Zr2 is Hf2).

TABLE 4. Selected bond distances (Å) for **1** and **2** (in brackets)[a]

M1–N1	2.465(5) (2.442(9))	M1–O1	1.961(4) (1.950(6))
M1–N2	2.442(5) (2.414(9))	M1–O2	2.233(4) (2.231(8))
M1–N3	2.461(5) (2.438(9))	M1–O3	2.170(4) (2.160(7))
M2–N4	2.408(5) (2.384(8))	M1–O4	2.241(4) (2.235(6))
M2–N5	2.480(5) (2.458(8))	M1–O5	2.123(4) (2.096(6))
M2–N6	2.473(5) (2.451(8))	M2–O1	1.975(4) (1.976(6))
M2–O6	2.259(4) (2.251(7))	M2–O7	2.151(4) (2.126(7))
M2–O8	2.121(4) (2.098(6))	M2–O9	2.266(4) (2.247(6))

[a] The atom numbering scheme is identical for **1** and **2**.

TABLE 5. Selected bond angles (°) for **1** and **2** (in brackets)[a]

N1–M1–N2	67.8(2) (69.5(3))
N1–M1–N3	67.9(2) (69.5(3))
N2–M1–N3	68.7(2) (69.8(3))
N1–M1–O2	67.8(2) (66.4(3))
N2–M1–O2	110.4(2) (111.1(3))
N3–M1–O2	131.5(2) (131.4(3))
N1–M1–O3	106.6(2) (106.9(3))
N2–M1–O3	69.6(2) (70.0(3))
N3–M1–O3	136.6(2) (137.9(3))
O2–M1–O3	75.2(2) (75.6(3))
N1–M1–O4	137.3(2) (135.9(3))
N2–M1–O4	144.3(2) (143.6(3))
N3–M1–O4	137.2(2) (136.4(3))
O2–M1–O4	72.6(1) (72.5(2))
O3–M1–O4	77.3(2) (76.5(2))
N1–M1–O5	82.1(2) (81.4(3))
N2–M1–O5	138.8(2) (139.2(3))
N3–M1–O5	74.3(2) (73.6(3))
O2–M1–O5	81.3(2) (80.5(3))
O3–M1–O5	149.1(2) (148.5(3))
O4–M1–O5	76.7(1) (76.9(2))
N1–M1–O1	142.0(2) (143.3(3))
N2–M1–O1	86.9(2) (86.7(3))
N3–M1–O1	76.9(2) (76.3(3))
O2–M1–O1	150.1(2) (150.3(3))
O3–M1–O1	89.2(2) (89.5(3))
O4–M1–O1	79.2(1) (79.2(2))
O5–M1–O1	102.0(2) (101.8(3))
M1–O1–M2	150.4(2) (151.3(3))

[a] Only one half of each dinuclear cation is considered here.

As has been pointed out above, the two acac ligands bound in a didentate fashion to one metal ion are inequivalent. Comparison of the metrical details of these two ligands shown in Fig. 3, where the averaged bond distances and angles for the two halves of the dication in **1** are given, reveals small, barely significant differences. The Zr–O_{acac} distances of the six-membered chelate rings I and II are different giving rise to a certain degree of asymmetry to both chelate rings. This asymmetry may be visualized by taking the difference of two Zr–O_{acac} distances within one ring: in I this difference is 0.134 Å whereas in II it is smaller (0.085 Å). This is in contrast to the structure of these chelate rings in $Zr(acac)_4$ [14] where crystallographic site symmetry requires *d*(Zr–O_{acac}) to be zero. That this observation is real is corroborated by the fact that the

TABLE 6. Structural details of the M–O–M unit in zirconium and hafnium

Complex	M–O_{oxo} (Å)	M–O–M (°)	Reference
$[(\eta^5\text{-}C_5H_5)_2Zr(CH_3)]_2O$	1.948(1)	174.1(3)	4
$[(\eta^5\text{-}C_5H_5)_2Hf(CH_3)]_2O$	1.941(3)	173.9(3)	2
$[(\eta^5\text{-}C_5H_5)_2ZrCl]_2O$	1.94(1); 1.95(1)	168.9(8)	3
$[\{((CH_3)_2Si)_2N\}_2Zr(CH_3)_2]_2O$	1.950	180.0	5
$[(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)]_2O$	1.968(3); 1.964(3)	165.8(2)	6
$[(\eta^5\text{-}C_5H_5)_2ZrO]_3 \cdot C_7H_8$ (av.)	1.959(3)	142.5(2)	12
$[\{LZr(acac)_2\}_2O]^{2+}$	1.961(4); 1.975(4)	150.4(2)	this work
$[\{LHf(acac)_2\}_2O]^{2+}$	1.950(6); 1.976(6)	151.3(3)	this work

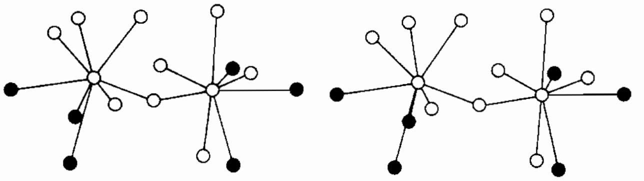


Fig. 2. Stereoview of the distorted dodecahedral polyhedra of the dications in **1** and **2** (open circles represent oxygen atoms and filled circles are nitrogen atoms).

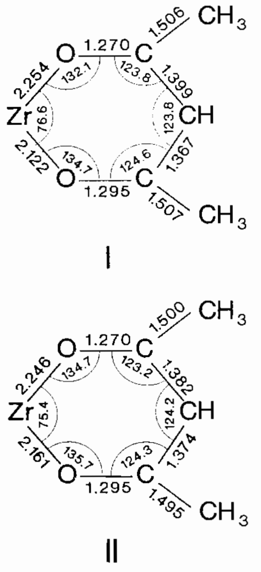
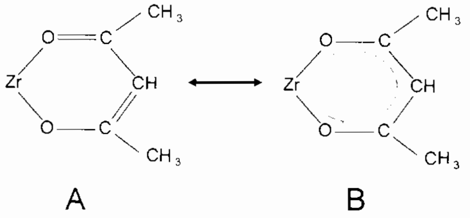


Fig. 3. Averaged structural details of the two coordinated acac⁻ ligands in **1**. I corresponds to the average of Zr1–O5–C15–C14–C13–O4 and Zr2–O8–C35–C34–C33–O9 rings and II to Zr1–O2–C8–C9–C10–O3 and Zr2–O6–C28–C29–C30–O7 rings.

same asymmetry is observed in **2** although here the larger e.s.d.s of this structure determination are of the same magnitude as the effect. Furthermore, the C=O distances within the chelate rings are different, the difference being 0.025 Å in both I and II. The C=O group with the shorter C–O bond is always coordinated more weakly to the Zr(IV) and Hf(IV) ions. The most significant difference between I and II are detected when comparing the two C–C distances within the six-membered chelate rings: in I the difference between the two is 0.032 Å whereas in II it is only 0.008 Å. Again, the same observation is made for **2**. Note that the C–CH_3 distances differ only insignificantly by 0.01 Å in I and 0.005 Å in II. Taking all these data together it is clear that I is more asymmetric than II in both structures but in both cases the sequence of alternating long–short bond distances is retained within the six-membered ring in agreement with the canonical structure A. Since the degree of asymmetry is different in I and II it is to be expected that the two tertiary protons give rise to two signals in the ^1H NMR spectrum. This has been observed. Similar inequivalence of two bound acac ligands in eight-coordinated Zr(IV) complexes has been reported previously for $Zr(acac)_2(NO_3)_2$ [15a] and $Zr(acac)_3NO_3$ [15b].



Supplementary material

Full tables of bond distances and angles, anisotropic displacement parameters, hydrogen atom positions, and F_o/F_c data for compounds **1** and **2**, and a perspective view of the dication in crystals of **2** are available from author K.W. upon request.

Acknowledgement

We gratefully acknowledge financial support of this work by the Fonds der Chemischen Industrie.

References

1 T. E. Macdermott, *Coord. Chem. Rev., 11* (1973) 1.

2 F. R. Tronczek, E. C. Baker, P. R. Sharp, K. N. Raymond, H. G. Alt and M. D. Rausch, *Inorg. Chem., 15* (1976) 2284.

3 J. F. Clarke and M. G. B. Drew, *Acta Crystallogr., Sect. B, 30* (1974) 2267.

4 W. E. Hunter, D. C. Hrncir, R. B. Bynum, R. A. Penttila and J. L. Atwood, *Organometallics, 2* (1983) 750.

5 R. P. Planalp and R. A. Andersen, *J. Am. Chem. Soc., 105* (1983) 7774.

6 J. L. Petersen, *J. Organomet. Chem., 166* (1979) 179.

7 G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 3, Pergamon, Oxford, 1987, p. 363.

8 K. Wieghardt, W. Schmidt, B. Nuber and J. Weiss, *Chem. Ber., 112* (1979) 2220.

9 G. V. Hevesy and M. Lögstrup, *Chem. Ber., 59* (1926) 1890.

10 *G. M. Sheldrick, SHELXTL-PLUS* program package; Universität Göttingen, FRG.

11 *International Tables of Crystallography,* Vol. IV, Kynoch, Birmingham, 1974, pp. 99, 149.

12 G. Fanchinetti, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc., 101* (1979) 1767.

13 M. C. Favas and D. L. Kepert, *Prog. Inorg. Chem., 28* (1981) 309.

14 J. V. Silverton and J. L. Hoard, *Inorg. Chem., 2* (1963) 243.

15 (a) V. W. Day and R. C. Fay, *J. Am. Chem. Soc., 97* (1975) 5136; (b) E. G. Muller, V. W. Day and R. C. Fay, *J. Am. Chem. Soc., 98* (1976) 2165.