Scientific paper

The Novel Crystal Structure with $Zr_6O_4(OH)_4$ Core and Hydrazine Carboxylate Ligands, and its Thermal Properties

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Dedicated to the memory of Prof. Dr. Marija Kosec.

Abstract

The title compound, $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}] \cdot 14H_2O$, was prepared with a novel multi-step synthetic pathway. The structure contains a $\{Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O_4)\}^{12+}$ core on which twelve hydrazine carboxylate anions are bound to form neutral coordination molecules. The coordination mode of carboxylate ligand is exclusively *N*,*O*-bidentate chelating, which is observed for the first time in this class of compounds. The title compound is also the first example of isolated Zr(IV) oxo clusters with cubic symmetry. The structure is stabilized with an extensive hydrogen bond network between coordination and water molecules, and amongst the solvent water molecules themselves. Thermogravimetric studies have shown that the prepared $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}] \cdot 14H_2O$ decomposed in several consecutive steps characterized by evolution of H_2O, CO, CO_2, N_2 and H_2, finally yielding ZrO_2. The decomposition mechanism is rather complex and includes the formation of a series of amorphous intermediates.

Keywords: Zr(IV) oxo clusters, hydrazine carboxylate, coordination chemistry, crystal structure, thermal analysis

1. Introduction

The chemistry of zirconium(IV) oxo clusters has witnessed considerable progress recently due to the extensive search for novel materials with interesting catalytic and other physical features, e.g. magnetic and optical.[1,2] One of characteristics of zirconium chemistry is the formation of oxo clusters. Till now, zirconium(IV) clusters containing three, four, five, six, eight and nine Zr(IV) ions were structurally characterized.[3] The most common are Zr_6 clusters that can link together into larger cores that contain 10, 12 or even 14 Zr(IV) ions.[3] A step from simple Zr(IV) ion to more complicated metal-containing clusters can lead to diverse products when combining with different organic ligands, ranging from simple isolated coordination molecules to porous materials as UiO-66 metal-organic framework.[4] On the other hand, some zirconium(IV) coordination compounds are interesting also as reactive zirconium precursors for preparation of fine zirconia powders (e.g. zirconium hydrazine carboxylate[5]), which decompose rapidly at relatively low temperatures in several consecutive exothermic autocatalytic steps.

The aim of our work was to determine the crystal structure and to study the thermal behaviour of zirconium hydrazine carboxylate (ZHC). The preparation and thermal properties of ZHC, formulated as $ZrO(N_2H_3COO)_2 \cdot 2H_2O$, have already been studied by several authors,[6–9] while its crystal structure remained unknown. The reason for this is probably to be found in the synthetic route of ZHC. Metal hydrazine carboxylates are normally formed by the reaction of aqueous solutions of corresponding metal salts with hydrazine carboxylic acid (N_2H_3COOH) previously dissolved in $N_2H_4 \cdot H_2O$.[7] The preparation of crystalline ZHC is not straightforward since zirconium species tend to form amorphous gels in an alkaline synthesis medium.[10] The single crystals suitable for X-ray structural analysis are difficult to obtain and even if the required product is obtained, it always contains some amorphous impurities. Consequently, we developed a new synthetic route that involved several consecutive steps including the preparation of ammonium zirconium hydroxide carbonate hydrate ($(NH_4)_6[Zr_2(OH)_2(CO_3)_6] \cdot 4H_2O$, AZC), which is water soluble and enables the preparation of basic zirconium solutions without the formation of amorphous gels. Surprisingly, the yield of the novel synthetic route was not

a simple ZHC but a compound with formula $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}] \cdot 14H_2O$. It is one of the first Zr-compounds with hydrazine carboxylate ligands and also the first $\{Zr_6(OH)_4O_4\}$ cluster with carboxylate ligands bound exclusively in a chelating mode. The descriptions of its crystal structure as well as its thermal properties are given in the paper.

2. Experimental

2. 1. Syntheses

2. 1. 1. Preparation of Hydrazine Carboxylic Acid

Hydrazine carboxylic acid was prepared by saturating hydrazine hydrate (100% solution, Acros Organics) with CO_2 at room temperature until white precipitate separated. The precipitate was filtered off and stored under CO_2 atmosphere.

2. 1. 2. Preparation of Ammonium Zirconium Hydroxide Carbonate Hydrate (AZC)

A saturated aqueous solution of ammonium carbonate (99.999%, trace metals basis, Sigma-Aldrich) was prepared at room temperature. Zirconium oxide chloride octahydrate $ZrOCl_2 \cdot 8H_2O$ (99.5% puriss, p.a., Sigma-Aldrich) was then added slowly into a vigorously mixed aqueous solution of ammonium carbonate with constant pH control of the mixture. The pH value of the reaction mixture lowered with the addition of $ZrOCl_2 \cdot 8H_2O$ until the pH value reached 8.5, which was then kept constant by alternating additions of $ZrOCl_2 \cdot 8H_2O$ and ammonium carbonate. After several cycles of alternating additions of both reagents, a white precipitate separated. The precipitate was filtered off and washed with ethanol. The composition of the white precipitate was confirmed as AZC with X-ray powder diffraction analysis (PDF #70-2149).

2. 1. 3. Synthesis of Zirconyl Hydrazine Carboxylate

A total of 15.12 g of AZC dissolved in 150 mL of water was added to hot (80 °C) aqueous solution of hydrazine carboxylic acid (42.0 g of hydrazine carboxylic acid dissolved in 200 mL of water). White crystalline solid (grains of ~1 mm in size) separated from the solution after several hours. The crystals were filtered off, washed with distilled water and dried under vacuum.

2. 2. Measurements

Hydrazine and zirconium content in the final white crystalline solid were determined volumetrically by titration with KIO_3 and EDTA complexometric titration, respectively. CHN microanalysis (PerkinElmer Series II CHNS/O Analyser 2400) was used to determine the amounts of C, H and N in the final product.

Thermoanalytical studies were carried out on Netzsch STA 409 system in synthetic air atmosphere (20 vol% O_2 and 80 vol% Ar) using ~100 mg samples and an Al_2O_3 crucible in a temperature range 30 °C–1000 °C. The heating rate for thermogravimetric, derivative thermogravimetric and differential thermal (TG-DTG-DTA) analysis was 10 K/min. For volatile products, evolved gass analysis (EGA) was coupled with mass spectrometry (MS; Pfeiffer PrismaPlus QMS 220) and gas chromatography (GC; Micro GC 3000A).

2. 3. X-ray Structure Analysis

For X-ray structure determination, the single crystals of final product were mounted on the tip of glass fibres and transferred to the goniometer head. Data were collected on a Nonius Kappa CCD diffractometer using monochromated Mo Kα radiation at room temperature with the use of Nonius *COLLECT* software.[10] Data reduction and integration were performed with the *DENZO-SMN* software package.[11] The initial structural model containing coordination molecule was obtained *via* direct methods using the *SIR97* structure solution program.[12] A full-matrix least-squares refinement on F^2 magnitudes with anisotropic displacement parameters for all non-hydrogen atoms using *SHELXL-97* was employed.[13] Oxygen atoms' positions from solvent water were subsequently obtained from a difference Fourier map and refined anisotropically. Due to the disorder of O6w, its coordinates and displacement parameters were not refined in the last cycles of refinement, and its disorder was not treated. Due to the proximity of several water molecules to symmetry elements and/or to other adjacent water molecules, their occupancies were fixed to 0.5. This makes the final structure physically and chemically reasonable, and the quantity of water is consistent with the results of elemental and thermal analyses. The value of goodness of fit (*S*, see Table 1) which deviates from 1.0 can be affected by the disordered water molecules in the crystal structure, and/or by pseudo-translational symmetry.

No H atoms except of these from hydrazine residue were initially located in difference Fourier maps. The positions of H atoms from hydrazine moiety were obtained from a difference Fourier map and refined using AFIX 3 command, i.e. only their displacement parameters were refined using the $U_{iso}(H) = 1.2U_{eq}(N)$ constraint. Figures depicting the structures were prepared with *ORTEP*3 and *Mercury*.[14,15]

CCDC-964930 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

3. 1. Thermal Analysis

TG-DTG-DTA-EGA-GC curves of the title compound are shown in Figure 1. The prepared compound decomposes in several consecutive steps with a final mass loss of 60.08%, which is very close to the calculated value (59.63%) when $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}] \cdot 14H_2O$ decomposes to ZrO_2. During the first interval of mass change (between 50 °C and 200 °C), the sample loses 19.48% of its original mass. Such relatively high mass loss cannot be a consequence of only a simple dehydration process, since dehydration itself should result in no more than 13.76% of mass loss. Instead, some parts of coordination molecules decompose as well in this early stage of thermal decomposition, which may be further indicated also from EGA analysis (Figure 1). More specifically, the detected volatile products between 50 °C and 200 °C are H_2O and some CO_2 (m/e 18 and m/e 44, respectively).

The second interval of mass loss proceeds over a broad range between 210 °C and 440 °C in which the sample loses 23.42% of its original mass. This value is close to the amount of hydrazine in the title compound (20.50%). However, according to the EGA results, volatile products accompanying thermal decomposition in this temperature interval are H_2O (m/e 18), CO_2 (m/e 44), H_2 (m/e 2) and gas with MS response at m/e 28, which was fixed as N_2 with GC analysis. Thus, the second stage of mass loss is not solely the dehydrazination process but a rather more complicated structure decomposition.

During heating above 440 °C, the sample continues to lose weight and more than one decomposition effect may be noticed between 440 °C and 750 °C with a total mass loss of 11.32%. Volatile products accompanying these decomposition effects again are fixed by EGA and GC analysis as H_2O, CO_2, H_2 and N_2.

The final stage of ZHC mass loss occurs between 750 °C and 850 °C where the sample loses 4.61% of its original mass. Contrary to the previous temperature interval, volatile products accompanying this stage are fixed by EGA and GC analyses as CO_2, CO and N_2, indicating that some intermediate products still containing nitrogen species decompose at rather high temperatures.

The observed decomposition path implies a rather complex mechanism that cannot be described by a series of simple stoichiometric reactions. Furthermore, intermediate products are amorphous and their exact chemical formulae are not known.

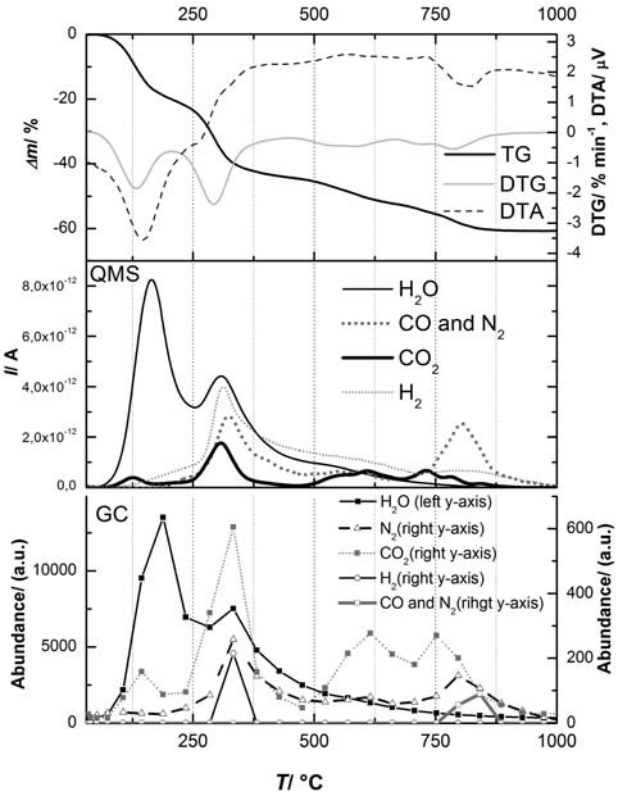


Fig. 1. TG-DTG-DTA-EGA-GC thermal decomposition curves of the title compound.

3. 2. Crystal Structure of Zirconyl Hydrazine Carboxylate $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}] \cdot 14H_2O$

Single crystal X-ray structure determination has shown that the title compound crystallizes in cubic *Fd*-3*c* space group (no. 228) in a unit cell with a = 29.2863(5) Å. The asymmetric unit (Fig. 2) consists of zirconium ion occupying a special position (twofold axis, Wyckof site 96*f*), hydrazine carboxylate moiety and two additional oxo ligands (O3 and O4). There are also four independent oxygen atoms that represent water molecules and are trapped in the voids of the structure. Details on crystal data, data collection and refinement can be seen in Table 1.

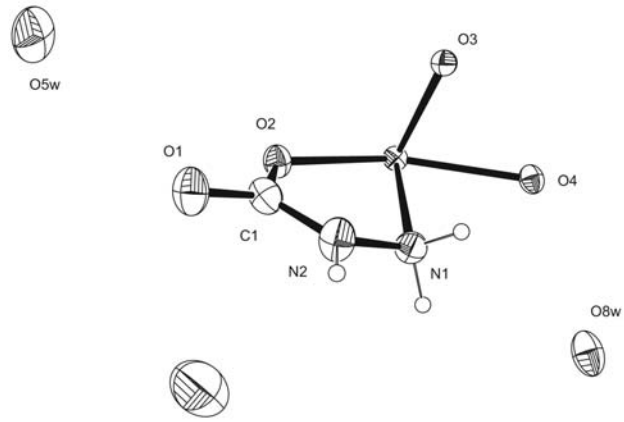


Fig. 2. The asymmetric unit of the title compound.

Table 1. Crystal data, data collection and refinement.

Crystal data	
Formula	$C_{12}H_{68}N_{24}O_{46}Zr_6$
M_r	1832.12
Cell setting, space group	Cubic, *Fd*-3*c*
a (Å)	29.2863(5)
V (Å^3)	25118.5(7)
Z	16
D_x (Mg m^{-3})	1.938
μ (mm^{-1})	1.079
F(000)	14656
Crystal form, colour	Cube, colourless
Crystal size (mm)	0.08 × 0.08 × 0.08
Data collection	
T (K)	293
Radiation type, wavelength	MoKα, 0.71073 Å
Diffractometer	Nonius Kappa CCD diffractometer
Data collection method	φ and ω scans
Absorption correction	Multi-scan
No. of measured, independent and observed reflections	4245, 1198, 735
Criterion for observed reflections	$F^2 > 2.0\ \sigma(F^2)$
R_{int}	0.016
θ range (°)	2.78–27.37
h range	–37→37
k range	–26→26
l range	–25→25
Refinement	
Refinement method	Full-matrix least-squares on F^2
R (on F_{obs}), *wR* (on F_{obs}), *S*	0.0515, 0.2361, 1.515*
No. of contributing reflections	1198
No. of parameters	72
No. of restraints	0
$(\Delta/\sigma)_{max}$, $(\Delta/\sigma)_{ave}$	0.003, 0.000
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	1.32, – 1.02

* The value of goodness of fit (*S*, see Table 1) which deviates from 1.0 can be affected by the disordered water molecules in the crystal structure, and/or by pseudotranslational symmetry.

3. 2. 1. Considerations About the Formula

The first challenge was to establish the formula of the newly synthesized compound, due to the unobserved hydrogen atoms. When applying symmetry on the asymmetric unit, the coordination core $\{Zr_6O_8\}^{8+}$ is obtained and surrounded by twelve $N_2H_3COO^-$ ligands, which leads to an anionic species $[Zr_6O_8(N_2H_3COO)_{12}]^{4-}$. For charge neutralization, hydrated Zr^{4+} cations or ammonium or hydrazinium cations may be present. The first option was unacceptable due to the size of $Zr(H_2O)_n^{4+}$, which is too large to settle into voids. However, it holds true that ammonia may be present in the reaction mixture and caught in the crystal structure due to the spontaneous decomposition of hydrazine and hydrazine carboxylic acid, but the probability for the presence of ammonium ions is relatively low due to the alkaline pH value, which retains most of ammonium species in the form of NH_3 molecules. Similar holds true for the possibility to find hydrazinium cations in the voids.

The second possibility was that the structure contains $\{Zr_6(OH)_8\}^{16+}$ cores surrounded by twelve $N_2H_3COO^-$ ligands, which would result in a cationic species $[Zr_6(OH)_8(N_2H_3COO)_{12}]^{4+}$. The positive charge may be neutralized by hydroxide anions in the voids. However, this is not very probable: there are no structures in CCDC[3] with any $Zr_6(OH)_8$ cationic species and charge-neutralizing OH^- anions.

Following the above two options, the cubic symmetry requirements of the presence of either eight oxo or eight hydroxo ligands that are arranged around six Zr(IV) ions were exhausted. Neglecting the symmetry, four oxo and four hydroxo groups besides the twelve $N_2H_3COO^-$ ligands should be present for electrostatic compensation. That would lead to isolated neutral coordination molecules $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}]$ around which molecules of the solvent may possibly be arranged. Such neutral molecules are common in the coordination chemistry of zirconium with different carboxylato ligands.[3] In an ideal case, it would be possible to distinguish between oxo and hydroxo oxygens on the basis of differences in Zr-O bond lengths. Our choice for the presence of both O and OH bridges is justified by the assumption of Piszczek et al.[16] that propose the migration of four protons between eight oxygen atoms, and the proposed formula including solvent water is also supported by the results of elemental and thermal analyses.

3. 2. 2. Coordination Molecules $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}]$

Zr and O atoms in a $\{Zr_6(OH)_4O_4\}^{12+}$ moiety lie in vertices of a rhombic dodecahedron (Fig. 3a). Zirconium atoms are coordinated with four oxygen atoms in the shape of a square pyramid while each oxygen is coordinated with three zirconiums in the shape of a trigonal pyramid. In other words, each oxygen atom represents a bridge between three Zr atoms (i.e. there are four μ_3-OH and four μ_3-O bridges). The distances Zr-O in the aforementioned moiety are 2.111(2) Å (to O3) and 2.215(3) Å (to O4), respectively. One would expect that one of the oxygen atoms (either O3 or O4) represents hydroxo and the other oxo bridges. Due to the small differences between both Zr-O bond lengths, we cannot differentiate between them. Zr-Zr are 3.4645(11) Å apart. The given distance ranges are similar as in other related compounds.[3] To the $\{Zr_6(OH)_4O_4\}^{12+}$ moiety, altogether twelve $N_2H_3COO^-$ anions are ligated, two on each Zr, in a bidentate chelating manner via N and O terminal atoms (Fig. 3b). The Zr-O2(ligand) and Zr-N distances are 2.210(4) and 2.454(5) Å, respectively, with the bite angle O2-Zr1-N1 of 66.55(16) °. Altogether, Zr(IV) ions are coordinated with

eight atoms (six O and two N) in a shape of a four-sided antiprism. The orientation of hydrazine carboxylate ligands attached to neighbouring Zr atoms is such that it enables the formation of intramolecular hydrogen bond, i.e. N1-H1A...O2^{i} with N1...O2^{i} distance of 2.857(8) Å [symm. code $i = y, z, x$].

To describe hydrogen bonding between the adjacent coordination molecules, firstly, $\{Zr_6(OH)_4O_4\}$ core should be represented in a different way, i.e. as an octahedron of six Zr atoms with additional eight oxygens lying above the side faces. The oxygens define a cube, i.e. a pair of two interpenetrating tetrahedra, one made of four O3 atoms and the other of four O4 atoms. The surroundings of O3 and O4 are not the same. Each O3 is surrounded by three hydrazine carboxylate ligands, and such four triples of the ligands give the tetrahedral shape to the coordination molecule. Each of its vertices is further connected by six moderately strong intermolecular hydrogen bonds to the neighbouring coordination molecules (N2-H2...O1^{ii} with the N2...O1^{ii} distance of 2.866(7) Å [symm. code $ii = -z, -x, -y$]). Thus a four-connected tetrahedral framework with large void volumes is formed, similarly as in the porous zeolite structures (Fig. 4).

3. 2. 3. Solvent Water Molecules

Voids that are formed in between the coordination entities contain water molecules. There are four of them in the asymmetric unit and altogether 14 per one coordination molecule. Void water molecules take part in the further formation of hydrogen bonds, i.e. with coordination molecules as well as with adjacent water molecules. As hydrogen atoms' positions were not obtained from a difference electron density map, only limited information

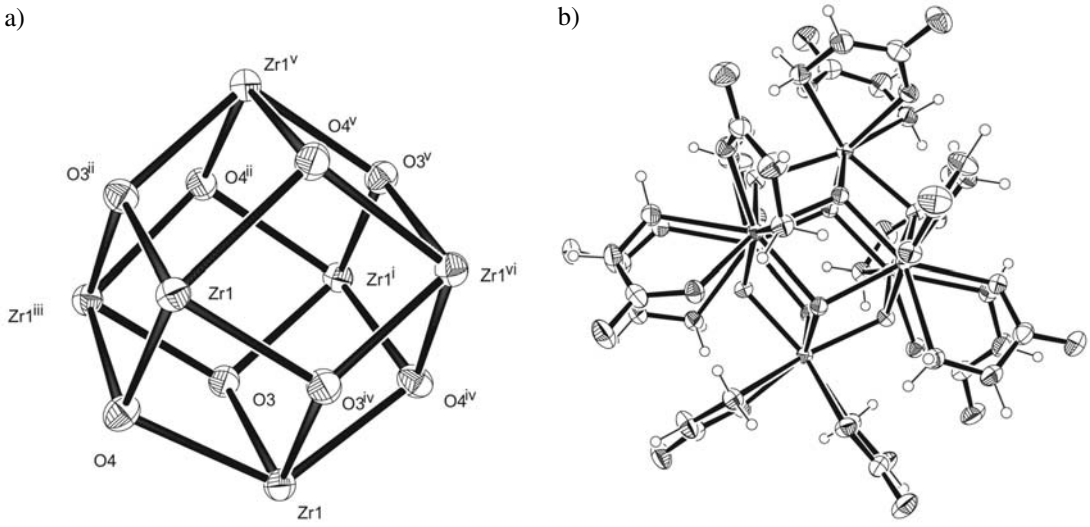


Fig. 3. The central core $\{Zr_6(OH)_4O_4\}^{12+}$ in which hydrogen atoms are omitted (a) and the coordination molecule $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}]$ (b).

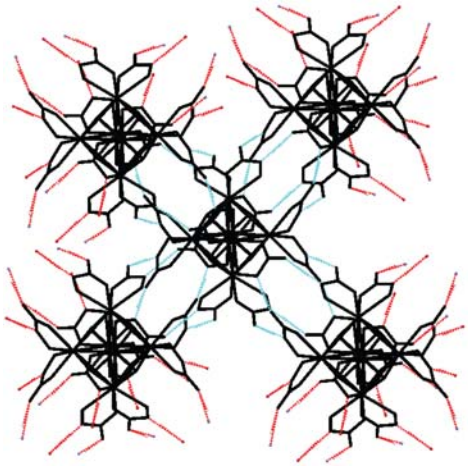


Fig. 4. Hydrogen bonding between the adjacent coordination molecules forming a 4-connected tetrahedral framework.

about hydrogen bonding can be given, i.e. only O...O distances. Fig. 5 represents the surroundings of each of the water molecules. At first sight, the surroundings of individual water molecules are too crowded, and are physically and chemically unreasonable. However, the occupancy of 0.5 for waters O5w, O6w and O8w solves this problem. The elongated displacement parameter of O6w was ascribed to its disorder; nevertheless, O6w was not refined as being disordered due to the quality of data (i.e. not trying to extract more information out of the data than possible). Details on solvent water molecules are collected in Table 2.

The composition of $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}] \cdot 14H_2O$ matches well with the results of chemical (elemental) analyses and weight loss in thermogravimetric study (Table 3); slight mismatches between the observed and expected wt. % are ascribed to analytical errors.

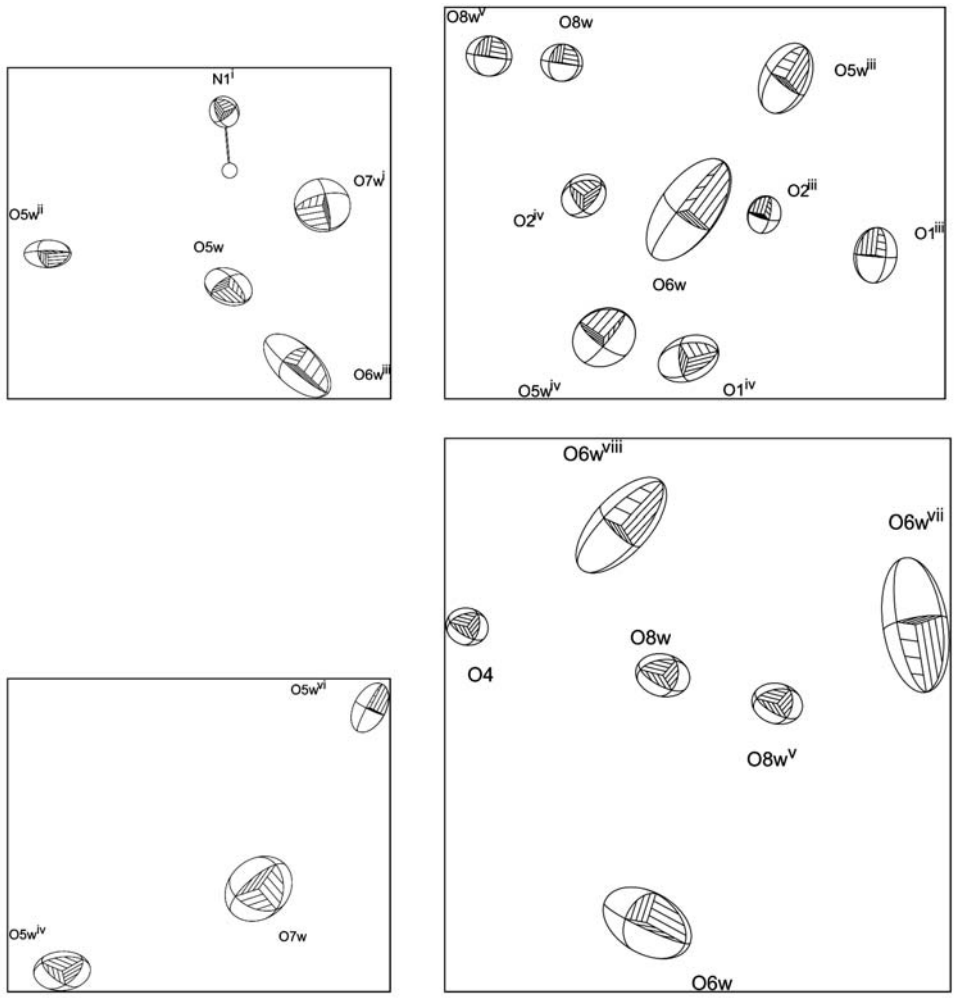


Fig. 5. The surroundings of the individual water molecules. For O...O distances and symmetry codes, see Table 3.

Table 3. Details on the surroundings of individual water molecules.

	Position (Wyckof site), occupancy	**No. in the unit cell**	**Closest neighbours & distances**
O5w	General (192*h*), 0.50	96	O5w^{ii} 3.08(3), O7w^{i} 2.975(14), N1^{i} 3.132(12) O6w^{iii} 2.124(15) if O5w is present, O6w will be absent
O6w	Special (96*g*), 0.50 [..2]	48	O1^{iii} and O1^{iv} 2.774(17) O8w or O8w^{v} 3.04(3) O2^{iii} and O2^{iv} 3.162(4) O5w^{iii} and O5w^{iv} 2.124(15) if O6w is present, both O5w will be absent
O7w	Special (48*d*), 1 [–4..]	48	O5w^{iv} and O5w^{vi} 2.975(14)
O8w	Special (64*e*), 0.50 [.3.]	32	O6w and/or O6w^{vii} and/or O6w^{viii} 3.04(3) O4 2.98(2) O8w^{v} 1.98(4) O8w is absent when O8w^{v} is present, and vice versa

Symm. codes: (*i*) *y*+1/4, –*x*, *z*–1/4; (*ii*) *z*+1/4, –*y*, *x*–1/4; (*iii*) –*x*+1/4, *y*, –*z*+1/4; (*iv*) –*y*, *x*–1/4, *z*+1/4; (*v*) –*x*, *z*–1/4, *y*+1/4; (*vi*) *y*+1/4, *x*–1/4, –*z*; (*vii*) –*z*+1/4, *x*, –*y*+1/4; (*viii*) *y*, –*z*+1/4, –*x*+1/4.

Table 3. Composition of the title compound.

Sample	Zr / %	N_2H_4 / %	C / %	H / %	N / %
obtained values from synthesized ZHC	29.40	20.50	7.88	4.09	17.56
calculated values from $Zr_6(OH)_4O_4(N_2H_3COO)_{12} \cdot 14H_2O$	29.88	20.97	7.86	3.71	18.35

3. 2. 4. Comparison with the Related Structures

CCDC[3] contains 44 records of the crystal structures that contain a $\{Zr_6(\mu_3\text{-}O)_8\}$ core surrounded by different carboxylato ligands. Such cores can link together into larger assemblies containing 10, 12 or 14 Zr atoms. There are ten compounds that consist of isolated building units $\{Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4\}$ with coordinated carboxylate ligands; nine of them contain neutral coordination molecules while only one contains a coordination cation electroneutralized by eight chloride anions and stabilized by eight solvent waters (refcode CUNTUB[17]). Such statistics again justify our decision for four oxo and four hydroxo groups in the coordination core (see section 3.2.1.).

Structures with neutral coordination molecules can be divided in two groups according to the coordination of the solvent (simple aliphatic alcohols or water):

A) structures that do not contain coordinated solvent (refcodes LEXTAK[16], LEXTEO[16], LELZOS[18] and REBNUH[19]), and

B) structures with coordinated solvent (refcodes FAPNEQ[20], FAPNIU[20], GOCXEB[21], GOCXIF[21], LELZUY[18]).

In the first two structures of group **A**, all twelve pivalic and 2,2-dimethylbutyric acid anions are bidentate bridging ligands. The coordination fashion of carboxylate anions in other two compounds of group **A** changes: nine ligands remain bidentate bridging while three coordinate in a bidentate chelating mode. In both cases, voids are formed: in LELZOS[18] they are occupied with the carboxylic acid molecules, while in REBNUH[19] the packing program suggests that there may be missing solvent.

Compounds of group **B** contain coordinated solvent and, with its presence, the coordination of carboxylate ligands becomes more diverse. In each structure, besides bidentate bridging and bidentate chelating mode, carboxylate ligands also bind monodentately. Diverse binding modes of carboxylate ligands might cause the formation of voids to become occupied only by carboxylic acid molecules and not with the solvent molecules as might be expected. Details can be found in Table 4.

Since the water molecules are not coordinated, the title compound belongs to group **A** of carboxylate compounds with $\{Zr_6(\mu_3\text{-}O)_8\}$ cores. Consequently, one would expect uniform or at least not very diverse coordination of hydrazine carboxylato ligands (at most two different coordination modes). As expected, all hydrazine carboxylato ligands are bidentate chelating ligands and such a coordination mode has not yet been observed for the related Zr(IV) clusters. The reasons for the hitherto unnoticed and uniform chelating mode for all twelve ligands might be hidden in the nature of the ligand that is capable to bind both *via* N and O-terminals, which is not true for simple carboxylates without additional functional groups. The obvious difference between the title compounds and the other compounds from Table 4 is also in the content of voids: usually these are filled with carboxylic acids, while only in our case do they only contain water (i.e. solvent) molecules. The explanation for this lies in the size of voids as well as in a fact that the water molecules are, in contrast to the molecules of carboxylic acids, capable of forming more hydrogen bonds due to their H-bond accepting and donoring features.

Table 4. The variety of coordination modes of carboxylate ligands in compounds with the isolated coordination core $\{Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4\}$.

Refcode	Carboxylate acid (RCOOH)	No. of μ_2-OOCR	No. of bidentate chelating O,O'	No. of monodentate O	Coordinated solvent	Content of voids
LEXTAK[16]	Pivalic acid	12	–	–	–	–
LEXTEO[16]	2,2-dimethylbutanoic acid	12	–	–	–	–
REBNUH[19]	Methacrylic acid	9	3	–	–	–
LELZOS[18]	5-norbornene-2-carboxylic acid	9	3	–	–	3 RCOOH
LELZUY[18]	5-norbornene-2-carboxylic acid	8	3	1	1 n-BuOH	3 RCOOH
FAPNEQ[20]	Isobutyric acid	8	3	1	1 H_2O	1 RCOOH
FAPNIU[20]	Isobutyric & methacrylic acid	2 iso + 6 met	1 iso + 2 met	1 iso	1 n-BuOH	1 iso 1 met
GOCXEB[21]	Methacrylic acid	8	3	1	1 PrOH	1 RCOOH
GOCXIF[21]	Benzoic acid	8	3	1	1 PrOH	1 RCOOH

4. Conclusions

The new compound with $\{Zr_6(OH)_4O_4\}$ core and hydrazine carboxylate anions was synthesized with a novel multi-step reaction route. The structural analysis revealed a building unit, i.e. $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}]$ coordination molecules in which twelve ligands are bound in a bidentate chelating manner to the central core, two of them on each Zr central ion, which had not been previously observed for this type of compound. The voids in between coordination molecules that are held together with hydrogen bonds are filled with water molecules that further stabilize the structure with additional hydrogen bonds. $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}] \cdot 14H_2O$ thermally decomposes in several consecutive steps. Volatile products evolving at different decomposition stages are H_2O, CO, CO_2, N_2 and H_2. The decomposition mechanism cannot be described by separate dehydration, dehydrazination and decomposition processes. Instead, some structure collapse takes place in the earliest stage, creating an amorphous intermediate product that undergoes a series of decomposition steps, and finally yields ZrO_2 above 850 °C.

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6. References

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Povzetek

Spojino $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}] \cdot 14H_2O$ smo pripravili po novi, večstopenjski sintezni poti. Struktura vsebuje $\{Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O_4)\}^{12+}$ jedro z dvanajstimi hidrazinkarboksilatnimi anioni, kar vodi do nastanka nevtralnih koordinacijskih molekul. Vseh 12 karboksilatnih ligandov se koordinira izključno na *N*,*O*-dvovezni kelatni način, ki pri podobnih spojinah do sedaj še ni bil opažen. Spojina predstavlja tudi prvi primer izoliranih okso-klastrov cirkonija(IV) kubične simetrije. K stabilnosti strukture doprinese razvejano omrežje vodikovih vezi tako med koordinacijskimi in vodnimi molekulami kakor tudi med samimi molekulami vode. Rezultati termogravimetričnih študij kažejo, da spojina $[Zr_6(OH)_4O_4(N_2H_3COO)_{12}] \cdot 14H_2O$ termično razpade v več zaporednih stopnjah, pri čemer nastanejo plinasti produkti H_2O, CO, CO_2, N_2 in H_2, trden preostanek pa predstavlja ZrO_2. Razpad spojine je precej kompleksen in vodi do tvorbe različnih amorfnih intermediatov.