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$[M_2(\mu-OH)_2(DHBQ)_3] \cdot (M = Zr, Hf)$ - two new isostructural coordination polymers based on

the unique M₂O₁₄ inorganic building unit and 2,5-dioxido-p-benzoquinone as linker

molecule

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Dedication to Professor Christoph Janiak on the Occasion of his 60th Birthday

Two new isostructural porous coordination polymers (CPs) were obtained under solvothermal reaction conditions using 2,5-1,2,4,5dihydroxy-p-benzoquinone (H₂DHBQ) or tetrahydroxybenzene (H₄THB) as linker molecule and Zr⁴⁺ or Hf⁴⁺ Highly crystalline compounds with composition salts. $[M_2(\mu-OH)_2(DHBQ)_3]$ ·x H₂O (M = Zr⁴⁺ or Hf⁴⁺, x = 0-3.6/3.3) were found in a wide temperature range (120-200 °C) and a reaction time of 70 h. The crystal structures were determined ab initio from powder X-ray diffraction data and the oxidation state of the linker was confirmed spectroscopically. The dinuclear inorganic building unit M₂O₁₄ is new for Zr- and Hf-CPs. For both compounds a full characterisation was carried out, i.e. crystal structure determination, spectroscopic measurements, elemental- and thermogravimetric analyses. $[M_2(OH)_2(DHBQ)_3]$ (M = Zr⁴⁺ or Hf⁴⁺) is stable up to 250 and 220 °C, respectively. Water sorption measurements proofed an uptake of 3.6 mol H₂O/mol and 3.3 mol H₂O/mol, respectively.

Introduction

Since the early 1990s the interest in coordination polymers (CPs) like coordination networks (CNs) as well as metal-organic frameworks (MOFs) is increasing.^[1] Coordination polymers are built up from inorganic building units (IBUs) interconnected with linker molecules.^[2] The coordination networks, a subclass of the CPs, exhibit a two- or three-dimensional interconnection to layers or networks. If the latter have a pore systems and organic linkers are used they are denoted as metal-organic frameworks (MOFs).^[2] These compounds have been very intensely investigated due to their potential application in separation or storage of gases^[3], in catalysis^[4] and as drug delivery systems^{[5][6]}.

In recent years, interest in Zr-based CPs has rapidly increased due to their high thermal and chemical stability^[7] as well as the low toxicity of Zr-salts^[8]. Mainly the use of carboxylate linker molecules was reported but also phosphonate linker molecules

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Supporting information for this article is given via a link at the end of the document. CCDC 2025008 and 2025009 contains the supplementary crystallographic data for $[M_2(\mu-OH)_2(DHBQ)_3]$ ·x H₂O (M = Zr⁴⁺ or Hf⁴⁺).

resulted in some highly porous compounds^[7]. The most common solvent for the synthesis of Zr-CPs is the teratogenic N,N-dimethylformamide (DMF) that contrasts with the low toxicity of Zr-salts. Due to this fact researchers recently tried to replace DMF through less toxic solvents such as formic acid, acetic acid, acetonitrile and water.^{[9]-[12]} This area of research is often named "green chemistry" and interest in this topic has increased drastically during the last few years.^{[13]-[15]}

A limited number of IBUs have been reported for Zr-CPs, which are summarized in Tab. S1. The most common IBU in carboxylate based Zr-CPs is the hexanuclear cluster with composition $\{Zr_6O_4(OH)_4\}^{[7]}$ described by KICKELBICK and SCHUBERT^[16] 1996 for the first time. Extended forms of this cluster are also known, namely the dodecanuclear cluster $\{Zr_{12}O_8(OH)_{20}(H_2O)_6\}^{[17]+[19]}$ and chains of condensed hexanuclear clusters^{[15][20]}. Furthermore, chains of edge-sharing ZrO₇-polyhedra^[21] or corner-sharing ZrO₆-octahedra^[22] have been reported.

Only few results on the synthesis of Zr-CPs employing catecholate or quinone linker molecules have been published. COOPER et al. reported the compounds MIL-151 to 154 (MIL = Matériaux de l'Institut Lavoisier) formed by the reaction of gallic acid, pyrogallic acid or salicylic acid and ZrCl₄. These compounds exhibit IBUs that consist of chains of edge sharing ZrO₈ polyhedra^[23]. The IBU is given in Figure 1 and the same IBU was found in the MOF MIL-163.^[24]

While CPs with 2,5-dioxylato-1,4-benzoquinone (DHBQ²⁻) as linker molecule (Fig. 2) and di- and trivalent metal ions such as Co^{2+} , Ni^{2+} , Cu^{2+} , Mn^{2+} , Fe^{2+} , Cr^{2+} , Ln^{3+} have been reported^{[25]–[29]}, for zirconium only molecular clusters are known. Thus two studies by MOUCHAHAM *et al.*^[30] and IMAZ *et al.*^[31] described compounds containing the anion [Zr(DHBQ)₄]⁴⁻ that are connected through hydrogen-bonds into a framework structure. An approach to get highly crystalline materials of composition $M(C_6H_2O_4)(H_2O)_2$ (M = Mg, or Zn) was reported by ABRAHAMS *et al.*^[32] who used 1,2,4,5-tetrahydroxy-benzene (H₄THB) instead of H₂DHBQ as a starting



Figure 1 Section of the IBU composed of edge sharing ZrO_8 polyhedra as found using the ligands gallic acid (H₄Gal) in MIL-153, -154 or 5,5'-(1,2,4,5-tetrazine-3,6-diyl)bis(benzene-1,2,3-triol) (H₆TzGal) in MIL-163: Zr-atoms are coloured in blue, carbon in black and oxygen in red.^{[25],[26]}

material (Fig. 2). The higher crystallinity was ascribed by the authors to a preceding in situ oxidation step leading to the quinone $DHBQ^{2}$.

Herein we present two new isostructural porous Zr- and Hf-CPs with a previously unknown IBU that were obtained using the linker molecules 2,5-dihydroxy-p-benzoquinone (H_2DHBQ) or 1,2,4,5-tetrahydroxy-benzene (H_4THB).



Figure 2 Redox chemistry of THB⁴⁻ (left) and DHBQ²⁻ (right).

Results and Discussion

Two new isostructural porous CPs of composition $[M_2(OH)_2(C_6H_2O_4)_3]$, with M = Zr⁴⁺ or Hf⁴⁺, were obtained at 120 or 200 °C using acetic acid, HCl, ZrCl₄ or HfCl₄ and the linker molecules 2,5-dihydroxy-p-benzoquinone or 1,2,4,5-tetrahydroxybenzene, respectively. During the synthesis optimization using our high-throughput set-up a slightly higher crystallinity of the products was observed using H₄THB as starting material instead of H₂DHBQ in a molar ratio of Zr:L:HCI:HOAc = 1.5:1:42:306 for H₂DHBQ and 1:1:33:67 for H₄THB, respectively. These results are line with the previously reported study of ABRAHAMS et al. [32]. While in the chemical system Zr⁴⁺/H₄THB/acetic acid several byproducts were observed (Fig. S2-3) most of the syntheses with HfCl₄ and H₄THB led to phase pure products. During synthesis optimization products with highest crystallinity could be obtain using high amounts of H₄THB and low amounts of HCI (Fig. S4) corresponding to a molar ration of Hf: L: HCI: HOAc = 1:2:27:78.

The structure solution and refinement were carried out using powder X-ray diffraction data from a $[Zr_2(OH)_2(C_6H_2O_4)_3]$ sample. Indexing, structure solution and Rietveld refinements were performed using TOPAS Academic 4.1^[33], EXPO 2009^[34] and Materials Studios^[35]. Details are described in the SI. The final Rietveld refinements against powder X-ray diffraction data of $[Zr_2(OH)_2(C_6H_2O_4)_3]$ and $[Hf_2(OH)_2(C_6H_2O_4)_3]$ are given in Figure 3 and S6. The crystallographic data of the Rietveld refinements are summarised in Table 1.

The structure exhibits an unusual IBU including M⁴⁺-ions that are coordinated by eight oxygen-atoms forming a distorted trigondodecahedron the same polyhedra as reported for MIL-151 - 154 and MIL-163^{[23],[24]}. Two of these polyhedra are linked by two μ -OH groups forming a dinuclear IBU (Fig. 4, top right). Although these were confirmed by IR spectroscopy, hydrogen atoms could not be refined but were added for charge balance. Each IBU is connected to six surrounding IBUs by six linker molecules (Fig. 4, top middle) to form a 3D network (Fig. 4, bottom right). The 1D channels with 1.9 x 2.3 Å diameter, taking

Table 1 Selected crystallographic data of	of the two isostructural compounds
$[M_2(OH)_2(C_6H_2O_4)_3]$ (M = Zr ⁴⁺ or Hf ⁴⁺).	

	[Zr ₂ (OH) ₂ (C ₆ H ₂ O ₄) ₃]	[Hf ₂ (OH) ₂ (C ₆ H ₂ O ₄) ₃]
crystal system	orthorhombic	orthorhombic
space group	Cccm	Cccm
a/Å	21.5158(6)	21.4455(6)
b/Å	6.7672(2)	6.7348(2)
c/Å	15.6894(4)	15.6205(5)
R _p / %	3.73	3.75
Rwp / %	5.31	5.26
GoF	2.80	2.71
R _{Bragg} / %	3.68	2.41

the van der Waals radii into account, along the *b*-axis are too small to be filled with molecules like N₂ with a kinetic diameter of 3.64 Å (Fig. 4, bottom left).^[36] The bond lengths are summarised in Table. S6. The distance between C-atoms varies between 1.28(6)-1.49(5) Å as expected for single and double bonds in the linker molecule (in all three possible oxidation states (Fig. 2)). From this structural data we cannot identify the oxidation state of the linker, unequivocally, but based on the results of the IR- and UV/Vis- spectroscopic measurements the presence of DHBQ²⁻ ions can be deduced. Due to the bridging character of the OHgroup the M-O1 bond (2.06(2)/2.09(2) Å) is slightly smaller than the other M-O bonds (2.177(9)-2.240(9) Å). Standard deviations are slightly higher for the linker molecule containing C4-C6 and O4 and O5 atoms compared to the linker molecule containing C1-C3 atoms.



Figure 3 Final plot of the Rietveld refinement of $[Zr_2(OH)_2(C_6H_2O_4)_3]$. The observed PXRD pattern (black), the calculated curve (red) and the difference plot (blue) are shown. The allowed peak positions are marked as black ticks below the curve.

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Figure 4 Crystal structure of [M₂(OH)₂(C₆H₂O₄)₃]: Asymmetric unit (top left), dinuclear cluster with (top middle) and without coordinating linker molecules (top right), space-filling model along *b*-axis (bottom left) and ball-and-stick model of the CN (bottom right) including the unit cell.

The results of the elemental analyses (Tab. 2) and the thermogravimetric measurements (Fig. 5 and S7) are in agreement with the composition of both compounds obtained from the crystal structure. Small deviations can be attributed to the different amounts of adsorbed water molecules molecules in the samples due to different temperatures used to dry the reaction products. Decomposition of $[Zr_2(OH)_2(C_6H_2O_4)_3]$ and $[Hf_2(OH)_2(C_6H_2O_4)_3]$ takes place at 250 and 220 °C, respectively. Further VT-PXRD measurements of $[Zr_2(OH)_2(C_6H_2O_4)_3]$ were performed and no phase transition was observed up to decomposition temperature (Fig. S8).



Figure 5 Left: TGA plot for $[Zr_2(OH)_2(C_6H_2O_4)_3] \cdot 2.5 H_2O$ showing the weight loss event occurring on evaporation of water molecules (7 %; expected 7 %) and above 250 °C the total structure decomposition (59 %; expected 57 %). Right: TGA plot for $[Hf_2(OH)_2(C_6H_2O_4)_3] \cdot H_2O$ showing the weight loss event occurring on evaporation of water molecules (3 %; expected 2 %) and above 220 °C the total structure decomposition (48 %; expected 47 %). The lower amount of adsorbed water in the pores compared to TGA-analysis of the Zr-compound can be attributed to a drying-step at 70 °C before the measurement.

Table 2 Comparison of the results of the CH-analysis with the theoretical data of $[M_2(OH)_2(C_6H_2O_4)_3]$ (with M = Zr and Hf). Samples were dried for several hours at 70 °C before the measurement.

r	C / % calc./ obs.	H / % calc./ obs.
[Zr ₂ (OH) ₂ (C ₆ H ₂ O ₄) ₃]	34.3 / 33.5	1.3 / 1.6
[Hf ₂ (OH) ₂ (C ₆ H ₂ O ₄) ₃]	26.9 / 26.3	1.0 / 1.5

IR-spectra of $[M_2(OH)_2(C_6H_2O_4)_3]$ (M = Zr⁴⁺ or Hf⁴⁺) are presented in Figure 6. The bands with low intensity at 3638 cm⁻¹ and 3645 cm⁻¹, confirm the presence of bridging µ-OH groups, respectively. Furthermore the bands corresponding to the OH deformation vibrations at 815 cm⁻¹ (Zr-OH) and 835 cm⁻¹ (Hf-OH), as well as the M-O stretching bands at 488 cm⁻¹ (Zr-O) and 493 cm⁻¹ (Hf-O) were observed in the IR spectra. The bands in the range of 1000-1700 cm⁻¹ are caused by C=O, C-O, C=C and C-C vibration modes and cannot be assigned unequivocally due to strong overlap of the bands.

To confirm the oxidation state of the linker molecule UV/Vis spectra were recorded. The UV/Vis-spectra of the two title compounds and H₂DHBQ are shown in Figure 7 (left). According to literature only the π - π * transitions of H₂DHBQ at 281 nm and 443 nm were observed^[37]. For the CPs these bands are shifted to 364 nm and 532 nm for [Zr₂(OH)₂(C₆H₂O₄)₃] and 346 nm and 530 nm for [Hf₂(OH)₂(C₆H₂O₄)₃]. No additional bands were observed in the spectra confirming the absence of any radical anions.



Figure 6 IR-spectra of $[M_2(OH)_2(C_6H_2O_4)_3]$ (M = Zr⁴⁺ or Hf⁴⁺) and the two linker molecules employed in this study.

To determine the porosity of $[M_2(OH)_2(C_6H_2O_4)_3] \cdot x H_2O$ (M = Zr⁴⁺ or Hf4+) samples were dried under reduced pressure (10-2 kPa) at 200 °C and used for nitrogen and water sorption measurements at 77 K and 25 °C, respectively. As expected, the isotherm of $[Zr_2(OH)_2(C_6H_2O_4)_3]$ confirms the sample to be nonporous against nitrogen (Fig. S9). The isotherms of water sorption measurements are given in Figure 7 (right) and Figure S10. They show a continuous water-uptake without any well-defined steps, which is probably due to the small pore size. The maximum capacity for water uptake is 3.6 mol/mol for [Zr₂(OH)₂(C₆H₂O₄)₃] and 3.3 mol/mol for [Hf₂(OH)₂(C₆H₂O₄)₃]. PXRD-measurements of the samples after the sorption measurements confirmed the stability of the samples (Fig. S11). Although the pores of $[M_2(OH)_2(C_6H_2O_4)_3]$ (M = Zr⁴⁺ or Hf⁴⁺) are very small, the structure seems to be flexible enough to incorporate water molecules at 25 °C.



Figure 7 Left: UV/Vis-spectra of $[Zr_2(OH)_2(C_6H_2O_4)_3]$ synthesized with H₄THB (black) and H₂DHBQ (red), [Hf₂(OH)₂(C₆H₂O₄)₃] (blue) and H₂DHBQ (green) (with NaCl as white standard). Right: Water sorption measurement of $[Zr_2(OH)_2(C_6H_2O_4)_3]$ (black) and [Hf₂(OH)₂(C₆H₂O₄)₃] (red) (right) . Adsorption is shown with filled, desorption with empty rectangles.

Stability of $[M_2(OH)_2(C_6H_2O_4)_3]$ (M = Zr⁴⁺ or Hf⁴⁺) in different solvents was investigated. Both compounds showed high stability while stored at RT under air for one year and during short-term treatment with toluene, acetone, DMF, ethanol and water. Details are given in section S8 in the supporting information.

Conclusions

The systematic investigation of the systems M4+/linker/HCI/HOAc with $M^{4+} = Zr^{4+}$ or Hf^{4+} , linker = H₂DHBQ or H₄THB in acetic acid as the solvent led to the discovery of two new isostructural porous CPs with composition $[M_2(OH)_2(C_6H_2O_4)_3]$ (M = Zr⁴⁺ or Hf⁴⁺). The crystal structure was elucidated from PXRD data and the presence of DHBQ2- linker molecules was demonstrated. Both compounds contain dinuclear edge-sharing polyhedra {M2O14} as the IBU, which has not been previously reported for Zr- or Hf-CPs. The use of H₄THB as starting material instead of its oxidized form H₂DHBQ leads to reaction products with higher crystallinity. This is probably due to an in-situ oxidation step. Both compounds show an incorporation of about 3.5 mol/mol water molecules, which demonstrates their porosity and makes these compounds the first Zr- and Hf-based porous CPs with the quinone linker molecule 2,5-dioxido-p-benzoquinone. It is notable that no acetate ions are incorporated into the final crystal structure although acetic acid had to be used as the solvent. This is in contrast to the chemistry of zirconium carboxylates, where acetic acid acts as a modulator^[38] or as a co-ligand^[39], which can lead to the formation of defect sites.^{[15][40][41]}

Experimental Section

Materials and methods

All chemicals were used as received without further purification. The high-throughput powder X-ray diffraction (PXRD) measurements for phase identification were performed using a Stoe Stadi P X-ray diffractometer containing an xy-stage and a Mythen detector and operating in transmission geometry ($CuK_{\alpha 1}$ radiation). PXRD patterns for structure determination were measured using a Stoe Stadi MP X-ray diffractometer operating in Debye Scherrer geometry using a Mythen detector (CuKa1 radiation). Thermogravimetric (TG) analyses were carried out using a Linseis STA 1600 analyzer with a heating rate of 4 K·min⁻¹ under flowing air (flow rate 100 sccm/min). For elemental analyses a EuroVector Euro EA elemental analyser was used and infrared spectra were measured on a Bruker ALPHA-P A220/D-01 FTIR spectrometer operating with an attenuated total reflection (ATR) unit. For sorption measurements a BELSORP-max (Bel Japan Inc.) devices and a temperature of 298 K (for water sorption) and 77 K (for N2-sorption) were used. Before sorption measurements, the samples were treated under reduced pressure (10⁻² kPa) and elevated temperature.

Synthesis

In house high-throughput (HT) multiclaves^[42] were used to systematically study the systems M⁴⁺/linker/additive/solvent, with M⁴⁺ = Zr⁴⁺ or Hf⁴⁺, linker = H₄THB or H₂DHBQ, additive = mainly HCl, NaOH, NaF and solvent = mainly DMF, water, acetic acid, methanol and toluene. The linker H₄THB was synthesized as previously described^[32]. Details can be found in the ESI, section S3. Only the use of acetic acid, ZrCl₄ and HCl lead to a highly crystalline product and is therefore described hereafter.

A total of 112 syntheses with 2,5-dihydroxy-p-benzoquinone (H_2DHBQ) and acetic acid as solvent were carried out using a

steel multiclave equipped with 24 Teflon reactors with a maximum solvent volume of 2 mL each. 260 syntheses with 1,2,4,5tetrahydroxybenzene (H₄THB) were performed using a steel multiclave equipped with 48 Teflon reactors with a maximum volume of 400 µL each. Acetic acid to HCI ratios were tested fixing the solvent volume at 1 mL and 200 µL, respectively. During the optimization process, i. e. by varying the chemical and process parameters, the optimized synthesis conditions were found using H₂DHBQ and H₄THB. The temperature was varied between 120 and 200 °C. The highest crystallinity was observed employing H₄THB as the linker molecule and a reaction temperature of 120 °C. For the Hf-based CP only the linker molecule H₄THB and a reaction temperature of 120 °C were used. The optimized synthesis conditions are given below. For the syntheses with H₄THB reaction "scale-up" to 1 mL reaction volume was performed. An overview of the high-throughput syntheses is given in the ESI, section S4.

Synthesis of [Zr₂(OH)₂(C₆H₂O₄)₃] with H₂DHBQ: 10.5 mg (75 µmol) H₂DHBQ and 11.6 mg (50 µmol) ZrCl₄ were added to a 2 ml Teflon insert and mixed with 875 µl glacial acetic acid and 175 µl HCl (37%). The reactor was closed, heated for 70 h at 200 °C and thereafter cooled down to room temperature within 10 h. The dark grey-brown product was filtered off and washed with methanol four times.

Synthesis of [Zr₂(OH)₂(C₆H₂O₄)₃] with H₄THB: 21.3 mg (150 µmol) H₄THB and 35 mg (150 µmol) ZrCl₄ were placed in a 2 ml Teflon insert and mixed with 582 µl glacial acetic acid and 418 µl HCl (37%). The reactor was sealed, heated for 70 h at 120 °C and thereafter cooled down to room temperature within 10 h. The dark grey-brown was filtered off and washed with methanol four times (yield: 19 mg).

Synthesis of [Hf₂(OH)₂(C₆H₂O₄)₃]: 42 mg (300 µmol) H₄THB and 48 mg (150 µmol) HfCl₄ were added to a 2 ml Teflon inlet and mixed with 666 µl glacial acetic acid and 334 µl HCl (37%). The reactor was closed, heated for 70 h at 120 °C and thereafter cooled down to room temperature within 10 h. The dark greybrown product was filtered off and washed with acetone four times (yield: 24 mg).

Keywords: metal organic frameworks (MOFs); zirconium; hafnium; crystal structure; dihydroxybenzoquinone

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Layout 1:

FULL PAPER

Two new isostructural porous coordination polymers were synthesized from $ZrCl_4$ or HfCl₄, HCl and the linker molecules H₂DHBQ or H₄THB in acetic acid as solvent. The structure was determined from PXRD data and full characterisation was performed.



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Page No. – Page No. Synthesis and characterisation of two new isostructural coordination polymers based on the unique M_2O_{14} inorganic building unit (M = Zr, Hf) and 2,5-Dioxylato-1,4benzoquinone as linker molecule

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