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ARTICLE

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PbADC and PbADC·H₂O: Two coordination polymers with acetylenedicarboxylate (ADC²⁻) as bridging ligand

Andrea Schuy^[a], Irena Stein^[a], and Uwe Ruschewitz^{*[a]}

Dedicated to Prof. Rüdiger Kniep on the Occasion of his 65th birthday.

Keywords: Acetylenedicarboxylate; Coordination Polymer; Crystal Structure; Lead; Topochemical Reaction

Single crystals of PbADC (**1**) and PbADC · H₂O (**2**) formed at the phase boundary of an aqueous silica gel containing acetylenedicarboxylic acid (HOOC-C≡C-COOH, H₂ADC) and an aqueous solution containing Pb(NO₃)₂. By choosing different concentrations of Pb(NO₃)₂ **1** and **2** were obtained as phase pure products. Additionally, **1** was obtained by grinding Pb(CH₃COO)₂ · 3 H₂O with H₂ADC resulting in a polycrystalline sample. The crystal structures of **1** (I4₁/amd, Z = 4; SrADC type structure) and **2** (P2₁/c, Z = 4, new structure type) were solved and refined from X-ray single crystal data. **1** exhibits a three-dimensional framework structure: Pb cations with a diamond-like arrangement are

interconnected by bridging ADC²⁻ ligands. In **2** double-layers are formed by Pb cations, bridging ADC²⁻ anions and water molecules. These layers are held together by hydrogen bonds via water molecules and oxygen atoms of the ADC²⁻ ligands. Suspending **1** for 24 h in water at ambient conditions leads to the formation of **2**, which can be converted to **1** again by careful dehydration at approx. 400 K in vacuum. This reversible reaction can be structurally interpreted as a topochemical reaction, which transforms a 3D coordination network into a 2D network structure and *vice versa*, as both crystal structures show noticeable structural similarities.

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Introduction

Coordination polymers and especially their porous exponents, frequently named MOFs (metal-organic frameworks) [1-3], are in the focus of many research groups world-wide. Their easy synthetic accessibility as well as their potential applications [4] have mainly caused this interest. Also the promise to “design” new solids starting from simple building blocks like metal ions or metal-oxo clusters and organic polyfunctional ligands [5] is attractive and another reason for the ongoing interest in coordination polymers. But despite some spectacular achievements [6] the synthesis of a new coordination polymer with an *a priori* given structural arrangement is in many cases difficult or even impossible.

In our work we have mainly concentrated on acetylenedicarboxylate (ADC²⁻), as this is one of the simplest linker, which can be used for the synthesis of coordination polymers. It consists of a rigid carbon backbone with two coordinating carboxylate groups. Thus, it is predestined to investigate the underlying mechanisms and interactions that lead to the formation of a specific structural arrangement. The first coordination compounds with ADC²⁻ were published by Robl [7–9]. In recent years we have been able to synthesize several hydrous [10–15] and anhydrous [16–19] coordination polymers with ADC²⁻ as bridging ligand, as well as compounds, which contain pyridine [20] or 4,4'-bipyridine [21] as additional ligands. Very recently it

was shown that ADC²⁻ can also be used to synthesize MOF-type coordination polymers [22,23]. With respect to structural design we found that a chain-like polymer as found in ${}^1_{}[M^{II}(H_2O)_4(ADC)_{2/2}] \cdot 2 H_2O$ can be converted to a 3D polymer as found in ${}^3_{}[M^{II}(H_2O)_2(ADC)_{4/4}]$ with M^{II} = Co [11], Ni [10] by removing water from the former compounds. It was also found that in compounds of composition ${}^1_{}[M^{II}(H_2O)_4(ADC)_{2/2}] \cdot 2 H_2O$ water can be replaced by pyridine (py) to give $[M^{II}(H_2O)_2(py)_2(ADC)_{2/2}]$ (M^{II} = Fe, Co, Ni [20]) without changing the characteristic structural arrangement. In all these compounds chain-like 1D polymers are formed. In the following we will present two new coordination polymers, namely PbADC (**1**) and PbADC · H₂O (**2**), with 3D and 2D network structures, which can be transformed to each other by a topochemical reaction.

Results and Discussion

PbADC (**1**) crystallizes in tetragonal space group I4₁/amd (no. 141) with Z = 4 (Table 1). It is isotypic with the crystal structure of SrADC [16]. The coordination sphere around Pb1 is shown in Figure 1. Each Pb atom is surrounded by eight oxygen atoms stemming from six different ADC²⁻ ligands. The resulting polyhedron can be described as a dodecahedron (D_{2d}). Two chelating carboxylate groups (Pb1-O1: 274 pm) and four monodentate coordinating oxygen atoms (Pb1-O1: 255.9 pm) are found. Each ADC²⁻ ligand coordinates to six Pb atoms with both carboxylate groups in a four-dentate bridging mode.

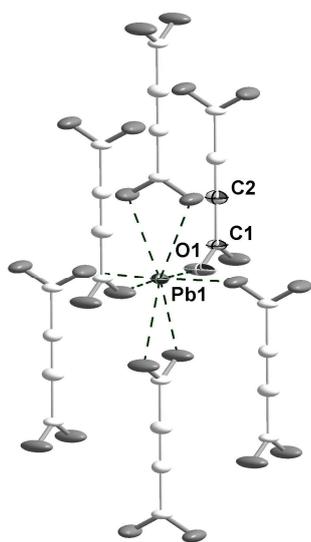


Figure 1. ORTEP diagram of the coordination sphere around Pb1 in PbADC (1) showing 50% probability thermal ellipsoids and the atom-numbering scheme. Pb-O bonds are drawn as broken lines.

The distances and angles within the ADC²⁻ ligand show the expected values (Table 2). Via ADC²⁻ ligands a 3D structure is formed, which may be formulated as $^{\infty}[\text{Pb}(\text{ADC})_6]_6$. This 3D structure is shown in Figure 2.

Table 1. Details of single crystal structural analysis of PbADC (1) and PbADC · H₂O (2).

	PbADC (1)	PbADC · H ₂ O (2)
Temperature	293(2) K	293(2) K
Formula	C ₄ O ₄ Pb	C ₄ H ₂ O ₅ Pb
Molecular weight	319.23 g·mol ⁻¹	337.24 g·mol ⁻¹
Space group	I ₄ /amd (No. 141)	P2 ₁ /c (No. 14)
Diffractometer	Stoe IPDS I	Stoe IPDS II
Radiation	MoK α	MoK α
Absorption correction	Numerical [24]	Numerical [24]
Formula units Z	4	4
Unit cell	a = 728.4(1) pm	a = 993.6(2) pm b = 400.70(4) pm c = 1032.5(2) pm
Volume	0.5478(2) nm ³	0.5686(2) nm ³ $\beta = 121.20(1)^\circ$
Density calculated	3.871 g·cm ⁻³	3.940 g·cm ⁻³
Crystal shape	plate	column
Crystal size	0.3 · 0.5 · 0.2 mm	1.0 · 0.7 · 0.6 mm
Crystal color	colorless	colorless
h k l range		
$h_{\text{min/max}}$	-9 / 9	-13 / 13
$k_{\text{min/max}}$	-9 / 9	-5 / 4
$l_{\text{min/max}}$	-13 / 13	-23 / 23
$2\theta_{\text{max}}$	56.3°	59.2°
Number of reflections:		
measured	2429	10471
independent	194	1594
μ	30.726 mm ⁻¹	29.624 mm ⁻¹
R-factors:		
$I_o > 2\sigma(I_o)$	R1 = 0.0241 wR2 = 0.0557	R1 = 0.0428 wR2 = 0.1091
all data	R1 = 0.0309 wR2 = 0.0572	R1 = 0.0484 wR2 = 0.1115

R _{int}	0.0998	0.1426
GooF = S _{all}	1.165	0.932
Number of refined parameters	18	92
F(000)	552	592
$\Delta\rho_{\text{min/max}}$	-0.927 / 1.139 Å ⁻³	-3.747 / 2.905 Å ⁻³

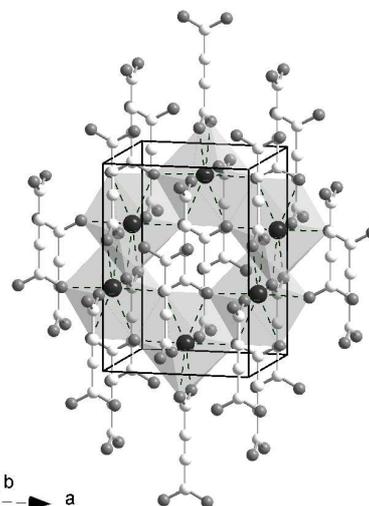


Figure 2. Packing diagram of PbADC (1) (Pb: large dark spheres, O: small grey spheres, C: small white spheres). Pb-O bonds are drawn as broken lines within each PbO₈ polyhedron.

Table 2. Selected interatomic distances [pm] and angles [°] in PbADC (1) and PbADC · H₂O (2).

PbADC (1)				
Pb1 – O1	255.9(9)	4 x	C1 – C2 – C2	180
	274(1)	4 x	O1 – C1 – O1	123(1)
Pb1 – Pb1	446.38(5)	4 x	O1 – C1 – C2	118.7(7)
C1 – C2	145(2)			
C2 – C2	120(3)			
C1 – O1	124(1)	2 x		
PbADC · H ₂ O (2)				
Pb1 – O42	258.8(7)		C1 – C2 – C3	171(1)
Pb1 – O41	259.4(7)		C2 – C3 – C4	174(1)
Pb1 – O11	263.2(7)		O11 – C1 – O12	124.9(9)
Pb1 – O3	265.4(7)		O41 – C4 – O42	123.6(8)
Pb1 – O12	265.6(6)		O11 – C1 – C2	118.0(9)
Pb1 – O11	269.3(7)		O12 – C1 – C2	117.1(8)
Pb1 – O3	271.8(7)		O41 – C4 – C3	117.4(8)
Pb1 – O42	274.8(7)		O42 – C4 – C3	119.0(9)
Pb1 – O11	294.5(7)			
Pb1 – Pb1	400.70(6)	2 x		
	442.08(8)	2 x		
C1 – C2	146(1)			
C2 – C3	122(1)			
C3 – C4	145(1)			
C1 – O11	127(1)			
C1 – O12	123(1)			
C4 – O41	128(1)			
C4 – O42	128(1)			

The Pb atoms are arranged in a diamond-like topology, as already described for SrADC [16]. The Pb-Pb distances (446.38 pm, 4x) and Pb-Pb-Pb angles (109.35°, 2x and 109.53°, 4x) are very close to the ideal values. This is already obvious from the unit cell of PbADC: $c/a = 1.4175$ is very close to $\sqrt{2}$ and $I4_1/amd$ is a direct subgroup of $Fd\bar{3}m$, the space group of diamond.

For SrADC a small negative thermal expansion was found below room temperature [16]. A so-called “guitar string” vibration [25] of an O atom connecting two Sr ions could be used as an explanation for this behavior. As obvious from Figure 1 a similar effect can be expected for PbADC, as the thermal ellipsoid of O1 shows an enhanced expansion perpendicular to the plain defined by Pb1-O1-Pb1. Indeed, $U_{11}(O1) = 1160(80) \text{ pm}^2$ is by a factor of 2-3 larger than the other U_{ii} values of oxygen and carbon. Preliminary low-temperature X-ray powder diffraction data do not show a significant shift of reflections in the temperature range 300 K – 260 K, i.e. a zero thermal expansion seems to occur. But it must be mentioned that PbADC shows a severe overlap of reflections, as $c/a = 1.4175$ is very close to $\sqrt{2}$. This makes the determination of unit cell volumes difficult and high resolution data are needed for a precise analysis. Below 260 K a reversible splitting of reflections is observed, which points to a phase transition, which has not been elucidated up to now. Both aspects will be investigated in future work.

PbADC · H₂O (**2**) crystallizes in monoclinic space group $P2_1/c$ (no. 14) with $Z = 4$ (Table 1). This crystal structure is unprecedented in the field of acetylenedicarboxylates. The coordination sphere around Pb1 is shown in Figure 3. Pb is coordinated to nine oxygen atoms stemming from five different ADC²⁻ ligands and two water molecules (Pb1-O3: 265.4 pm and 271.8 pm, resp.). The polyhedron can best be described as a 4,4,4-tricapped trigonal prism. Two carboxylate groups of the ligand bind in a chelating mode (258.8 – 269.3 pm) and three oxygen atoms in a monodentate way (263.2 – 294.5 pm). Each ADC²⁻ ligand coordinates to five Pb atoms. The distances and angles within the ADC²⁻ ligand are in the expected range (Table 2).

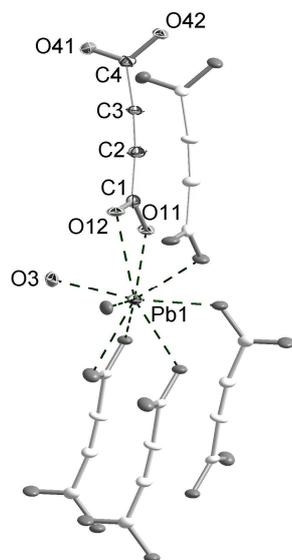


Figure 3. ORTEP diagram of the coordination sphere around Pb1 in PbADC · H₂O (**2**) showing 50% probability thermal ellipsoids

and the atom-numbering scheme. Pb-O bonds are drawn as broken lines. Positions of hydrogen atoms could not be determined.

Via these ADC²⁻ ligands double layers are formed, which can be seen in Figure 4. These layers are held together by hydrogen bonds, which include the water molecules (O3) and oxygen atoms of the carboxylate groups (O3-O41: 273 pm; O3-O12: 274 pm). Thus, the structure of **2** can be better formulated as ${}^2_x[\text{Pb}(\text{ADC})_{5/5}(\text{H}_2\text{O})]$. The Pb-Pb distances (400.70 pm, 2x and 442.08 pm, 2x) differ from those found in **1**, as the arrangement of the Pb atoms is completely different with double chains parallel to [010] being formed.

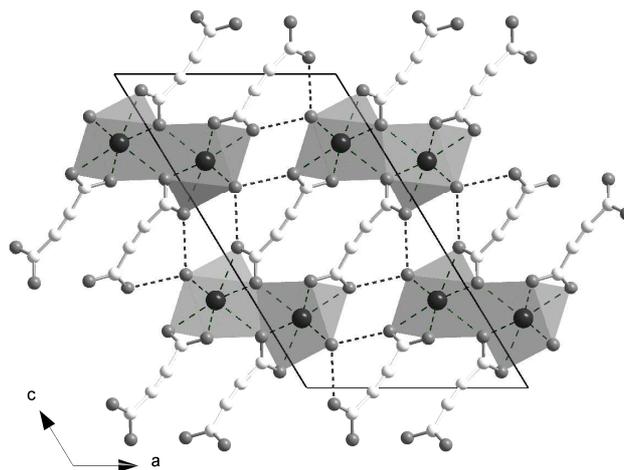


Figure 4. Packing diagram of PbADC · H₂O (**2**) in a projection along [010] (Pb: large dark spheres, O: small grey spheres, C: small white spheres). Pb-O bonds are drawn as broken lines within each PbO₉ polyhedron, hydrogen atoms have not been located. Hydrogen bonds between oxygen atoms are drawn as dark dotted lines.

In Figure 5 projections of the crystal structures of **1** and **2** are shown. In these projections intriguing similarities are found. Accordingly, H₂O molecules act as scissors, which cut double layers out of the 3D structure of **1**. The arrangement of the ADC²⁻ ligands seems to be almost unchanged. This reminds of an intercalation reaction as found for graphite and alkali metals. But here, Pb-O bonds are broken and replaced by new Pb-OH₂ and hydrogen bonds. Of course, this picture is simplifying, as only a projection (Figure 5) is considered. The situation is somewhat more complicated, if bonds perpendicular to the projection plane and the changing arrangement of the Pb atoms (see above) are also taken into account.

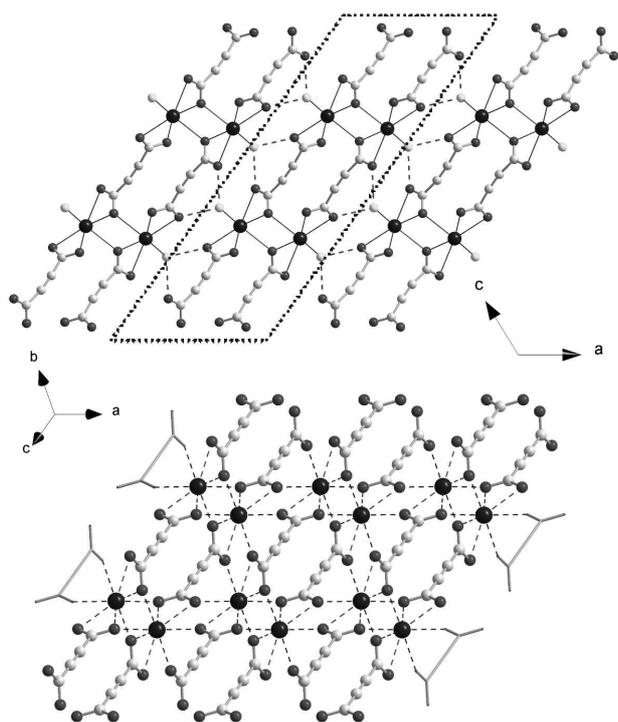


Figure 5. Projections of the crystal structures of $\text{PbADC} \cdot \text{H}_2\text{O}$ (**2**) (above; projection along $[010]$; one ${}^2[\text{Pb}(\text{ADC})_{5/5}(\text{H}_2\text{O})]$ double layer is emphasized) and PbADC (**1**) (below; projection along $[111]$); colors and symbols are the same as used in Figure 4. For comparison reasons, some ADC^{2-} ligands in **1** are given as wires.

To prove that **1** and **2** are topochemically related it was attempted to reversibly remove water from the crystal structure of **2**. DTA/TG investigations (Figure 6) show that the release of water starts at approx. 400 K. The calculated mass loss (5.3 %) is in reasonable agreement with the observed value (6.8 %). The dehydration is accompanied by a broad endothermic signal indicating a slow process. At approx. 525 K a further mass loss of 46.5 % is observed. Assuming that all light elements (C, O) are released and elemental Pb remains, a theoretical (maximal) mass loss of 33.2 % is calculated. Therefore it must be assumed that some sample was expelled from the DTA/TG container due to a heavy decomposition of PbADC . This is confirmed by the unusual DTA curve as well as by the overswinging of the TG signal. A similar decomposition was observed for Tl_2ADC [19], where elemental Tl formed as the final product. Compared to SrADC [16], PbADC shows a much lower thermal stability. SrADC starts decomposing at approx. 750 K under comparable conditions. This is in agreement with other observations we made for acetylenedicarboxylates: compounds with noble metals show a low thermal stability, whereas alkali and alkaline earth metal compounds are much more stable. $[\text{Cu}(\text{ADC})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ [13] already decomposes at ambient conditions; attempts to synthesize an Ag-acetylenedicarboxylate failed up to now, as almost immediately a black precipitate formed, which mainly consists of elemental Ag. Thus, acetylenedicarboxylic acid seems to be a good reducing agent for cations of noble metals.

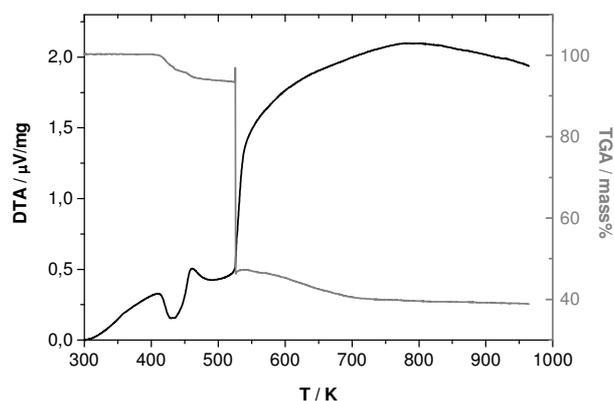


Figure 6. $\text{PbADC} \cdot \text{H}_2\text{O}$ (**2**): DTA (black) and TG (grey) curves.

The DTA/TG analysis of $\text{PbADC} \cdot \text{H}_2\text{O}$ (**2**) revealed a water loss starting at approx. 400 K. This was corroborated by XRPD data (Figure 7). A sample of **2** was evacuated at room temperature for two days. The resulting powder only shows reflections of **2**. Another sample heated at 378 K in vacuum for four days already gave a powder diffraction pattern, where **1** next to **2** was detected. The amount of **1** is increased in a sample heated at 398 K in vacuum for one day. A phase pure sample of **1** was obtained after heating in vacuum at 398 K for seven days. To exclude any influence of moisture in this investigation all sample handling was carried out in an argon atmosphere and for the XRPD measurements the samples were filled in capillaries in a glove box (argon atmosphere). Due to the strong absorption of Pb the quality of the resulting diffraction patterns is modest (Figure 7), but the formation of **1** and/or **2** can clearly be seen in the patterns.

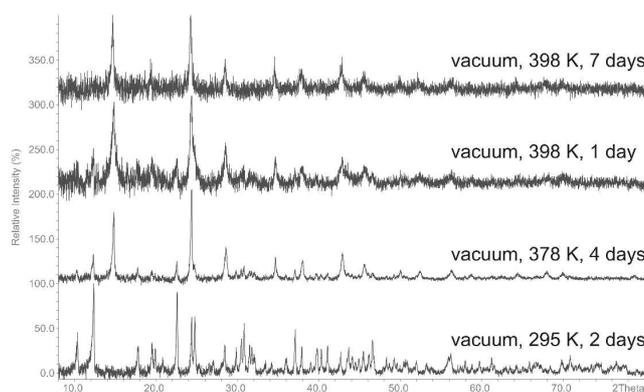


Figure 7. Background corrected X-ray powder diffraction patterns (Huber G670, $\text{CuK}\alpha_1$ radiation, capillary) of $\text{PbADC} \cdot \text{H}_2\text{O}$ (**2**) upon heating in vacuum.

To prove the reversibility of the hydration/dehydration process a sample of **1** as obtained from a mechanochemical synthesis was exposed to air for 60 h. The XRPD pattern of the resulting sample only showed reflections of **1** with no obvious reflection broadening or decrease of reflections' intensities. This is somewhat surprising, as it was noticed that single crystals of **1** lost their transparency, when exposed to air. Obviously, the exposure to air does not lead to a detectable formation of **2**, at least not in the time scale (60 h) investigated. Another sample of **1** was suspended in water. After 24 hours at room temperature the suspension

was filtered and investigated by XRPD. The resulting powder only gave reflections of **2** with surprisingly small reflection widths indicating a very good crystallinity of the sample (Figure 8). Thus, the dehydration of **2** to form **1** (398 K, vacuum for several days) is completely reversible at room temperature:

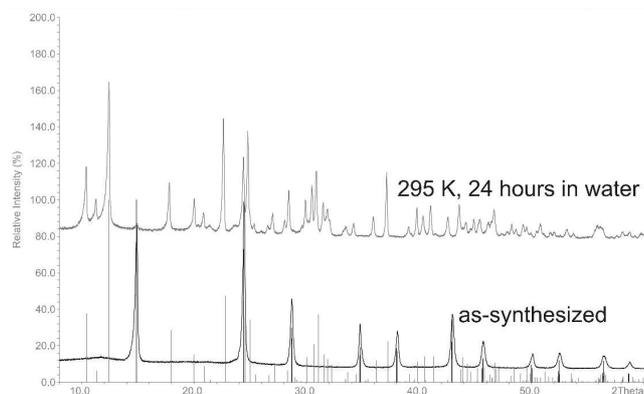
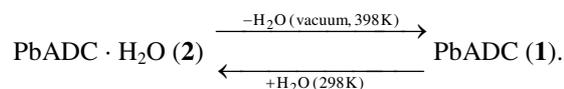


Figure 8. X-ray powder diffraction patterns (Huber G670, $\text{CuK}\alpha_1$ radiation, flat sample) of PbADC (**1**) as-synthesized (black curve) and after suspending in water for 24 hours (grey curve). As a guide for the eye the theoretical patterns of PbADC \cdot H₂O (grey) and PbADC (black) are shown as line diagrams.

Conclusions

The topochemical reaction, which converts PbADC (**1**) in PbADC \cdot H₂O (**2**) and *vice versa*, is unprecedented in the field of coordination polymers with ADC²⁻ as bridging ligand. For [Ce₂(ADC)₃(H₂O)₆] \cdot 2 H₂O it was found that two lattice water molecules can be removed with retention of the crystal structure [26]. This dehydration can be followed in a single-crystal-to-single-crystal manner. However, only weakly bound lattice water molecules are removed, whereas in **2** a coordinated water molecule is removed, which leads to a change in the dimensionality of the polymeric network from 2D to 3D and *vice versa*. Additionally, new coordinating bonds with the ADC²⁻ ligand are formed, but the over-all structural arrangement only changes very little, as can be seen in Figure 5.

The topochemical reaction of **1** with water can also be described as an intercalation: H₂O is intercalated between two double layers of ${}^2_\infty[\text{Pb}(\text{ADC})_{5/5}]$. In one of our current research projects we are trying to replace water by other polar and more bulky molecules to obtain a 2D coordination polymer connected by pillars, which should lead to a compound with pores between the layers. These investigations include the replacement of water in **2** by bulky donor molecules and the reaction of **1** with these molecules.

It is noteworthy that both **1** and **2** were obtained as phase pure and single-crystalline samples by a very similar procedure, the so-called gel method, just by changing the concentration of Pb(NO₃)₂ in the upper aqueous solution. A higher concentrated Pb(NO₃)₂ solution (*c* = 1 mol/l) leads to PbADC (**1**), whereas a lower Pb(NO₃)₂ concentration (*c* = 0.4 mol/l) leads to PbADC \cdot H₂O (**2**). It seems to be

worthwhile to check whether this finding can be transferred to other coordination polymers to synthesize compounds with different water contents.

Experimental Section

Synthesis. PbADC (**1**) and PbADC \cdot H₂O (**2**) are synthesized at the phase boundary of an aqueous silica gel containing acetylenedicarboxylic acid (HOOC-C \equiv C-COOH, H₂ADC) and an aqueous solution containing Pb(NO₃)₂.

PbADC (**1**): a) 2 ml HNO₃ (2 M) were added to 10 ml of an aqueous solution of acetylenedicarboxylic acid (0.570 g, 5 mmol; Fluka, > 98 %). A pH of approx. 5.5 was adjusted by adding an aqueous Na₂Si₃O₇ solution ("Sodium water-glass", Fluka). The forming gel was layered with 10 ml of an aqueous solution of Pb(NO₃)₂ (3.312 g, 10 mmol; Riedel-DeHaën, > 99 %). At the phase boundary colorless crystals of **1** grew within several days. These crystals were isolated and washed with ethanol and ether. They were stored in an argon atmosphere, as after several days in air the crystals lost their transparency and became milky. According to X-ray powder diffraction data (Huber G670, $\text{CuK}\alpha_1$ radiation, flat sample) the isolated samples are phase pure. No yield was determined.

b) Polycrystalline samples of **1** were also synthesized by grinding Pb(CH₃COO)₂ \cdot 3 H₂O (0.382 g, 1.006 mmol; Sigma-Aldrich, > 99.99 %) and H₂ADC (0.117 g, 1.029 mmol; Fluka, > 98 %) in a mortar with a pestle. The smell of released acetic acid indicates the proceeding of the reaction. At the beginning of the grinding procedure the sample becomes wet and creamy, but after a few minutes of grinding a dry product is obtained. According to X-ray powder diffraction data (Huber G670, $\text{CuK}\alpha_1$ radiation, flat sample) the isolated samples are phase pure. This is confirmed by elemental analysis: calc. for C₄O₄Pb (319.24): C 15.05 %; found: C 14.78 %, H 0.12 %. The conversion is quantitative.

PbADC \cdot H₂O (**2**): 2 ml HNO₃ (2 M) were added to 10 ml of an aqueous solution of acetylenedicarboxylic acid (0.570 g, 5 mmol; Fluka, > 98 %). A pH of approx. 5.5 was adjusted by adding an aqueous Na₂Si₃O₇ solution ("Sodium water-glass", Fluka). The forming gel was layered with 25 ml of an aqueous solution of Pb(NO₃)₂ (3.312 g, 10 mmol; Riedel-DeHaën, > 99 %). At the phase boundary colorless crystals of **2** grew within ten days. These crystals were isolated and washed with ethanol and ether. According to X-ray powder diffraction data (Huber G670, $\text{CuK}\alpha_1$ radiation, capillary \varnothing 0.3 mm) the isolated samples are phase pure. This is confirmed by elemental analysis: calc. for C₄H₂O₅Pb (337.26): C 14.25 %, H 0.59 %; found: C 14.36 %, H 0.46 %. No yield was determined.

Topochemical reactions: **2** was heated in a Schlenk flask in a dynamic vacuum. At different conditions (reaction time, temperature) samples were investigated *ex-situ* by X-ray powder diffraction (Huber G670, $\text{CuK}\alpha_1$ radiation, capillary \varnothing 0.3 mm). To prevent the sample from the exposure to air and moisture all handling was carried out in a glove box (Argon atmosphere). **1** was exposed to air for several days as well as suspended in water for several days and at different temperatures. The resulting samples were investigated by X-ray powder diffraction (Huber G670, $\text{CuK}\alpha_1$ radiation, flat sample).

X-ray single crystal structure analysis. Single crystals of **1** and **2** were isolated as described above and mounted in sealed glass capillaries on a Stoe IPDS I (**1**) or Stoe IPDS II (**2**) single crystal diffractometer (*T* \approx 293 K, MoK α radiation). For data collection and reduction the Stoe program package [27] was applied. The

structural models were solved using SIR-92 [28] and completed using difference Fourier maps calculated with SHELXL-97 [29], which was also used for final refinements. All programs were run under the WinGX system [30]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the water molecule in **2** could not be located in Fourier maps and were therefore not included in the final refinement. More details of the structural analysis [31] are given in Table 1. Selected interatomic distances and angles are listed in Table 2. The single crystal of **2** is quite large, but still fits the beam size of the diffractometer, as was checked with the built-in camera. The numerical absorption correction gave reasonable results ($R_{\text{int}} = 0.1426$), but the resulting residual electron density is much larger than for **1**. Attempts to isolate smaller single crystals of **2** to obtain an improved structural analysis, were not successful.

Thermoanalytical Investigations. A DTA/TG investigation was performed on PbADC · H₂O (**2**) in the temperature range 298–973 K using a Netzsch STA 409C housed in a glove box (M. Braun, Garching/Germany), heating rate 10 K/min.

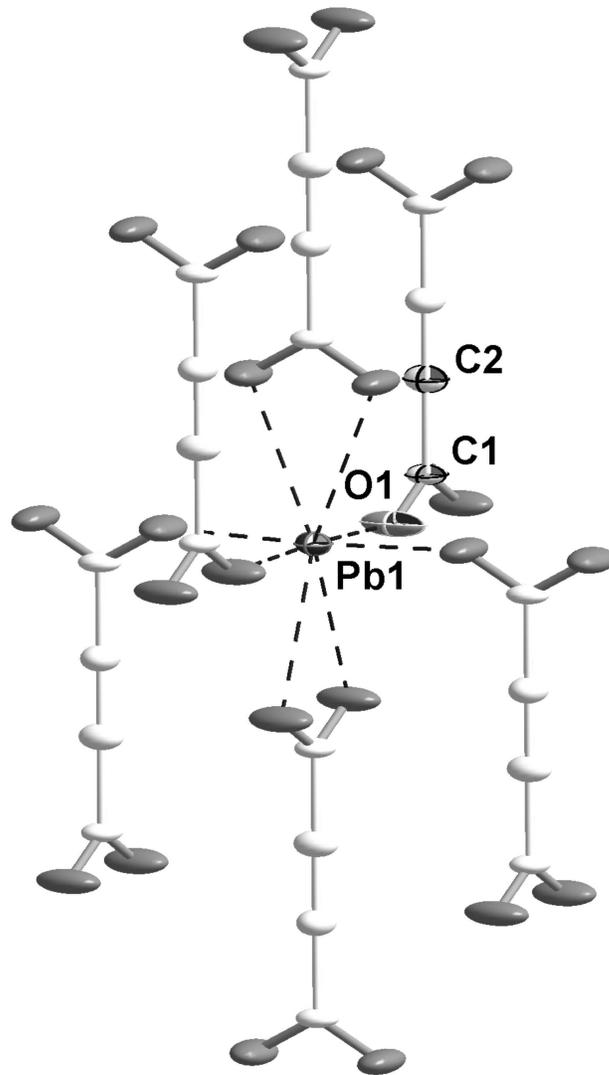
Acknowledgments

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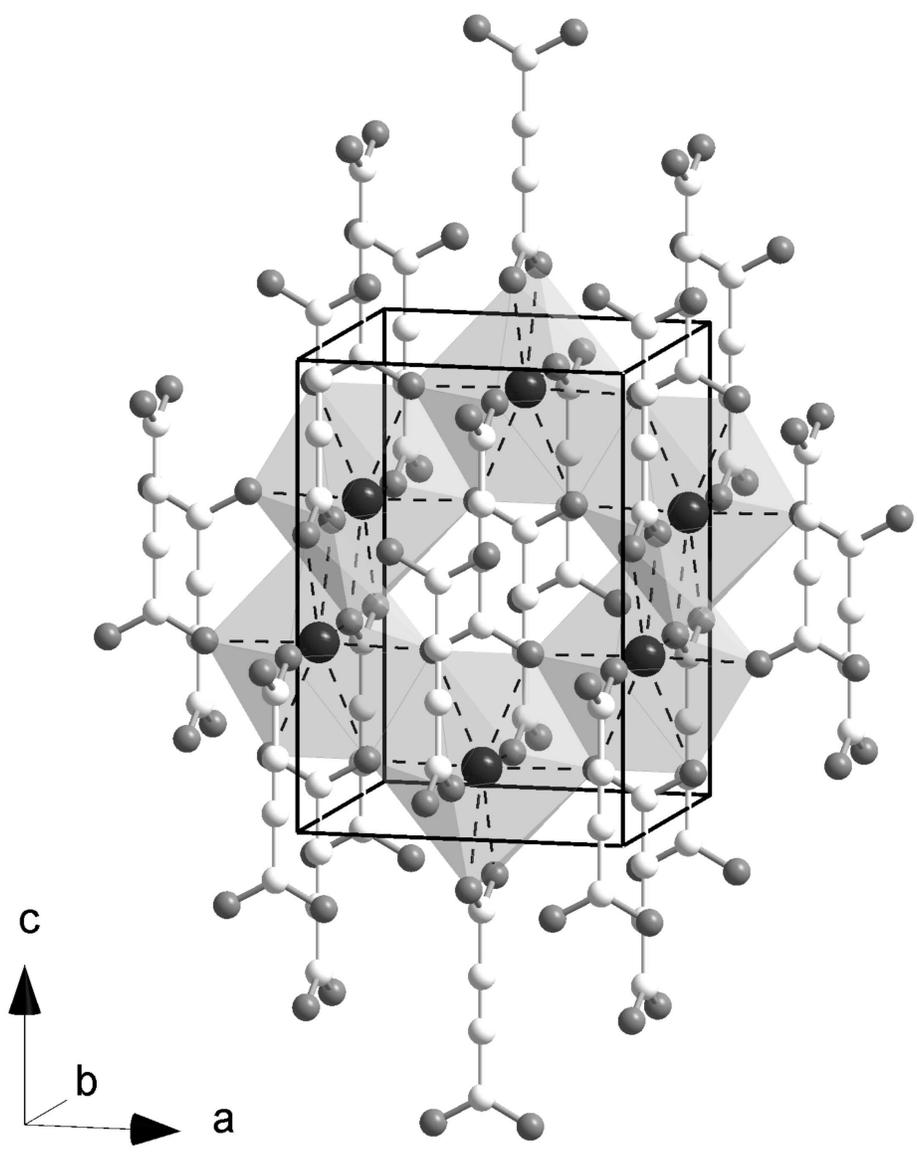
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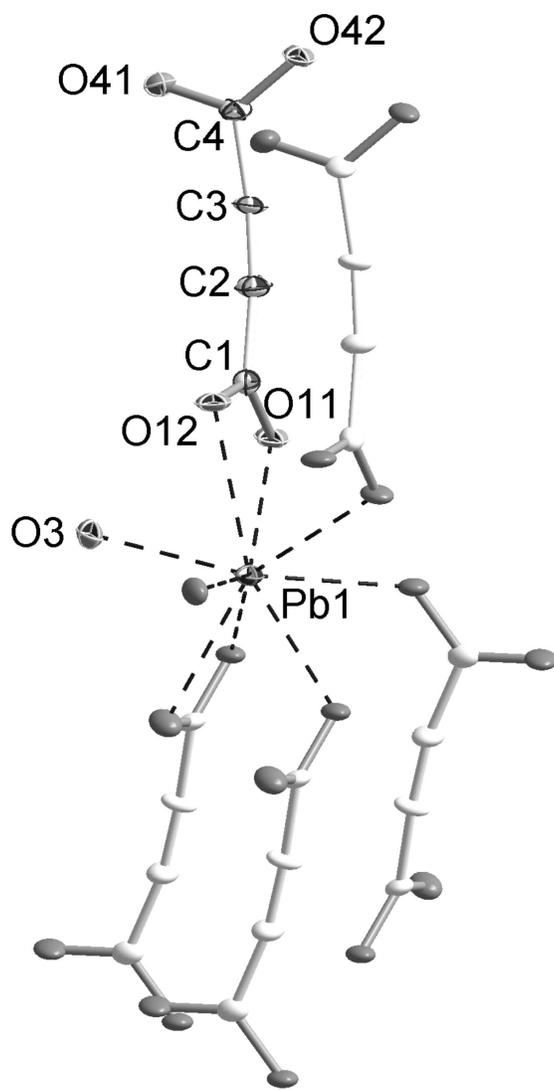
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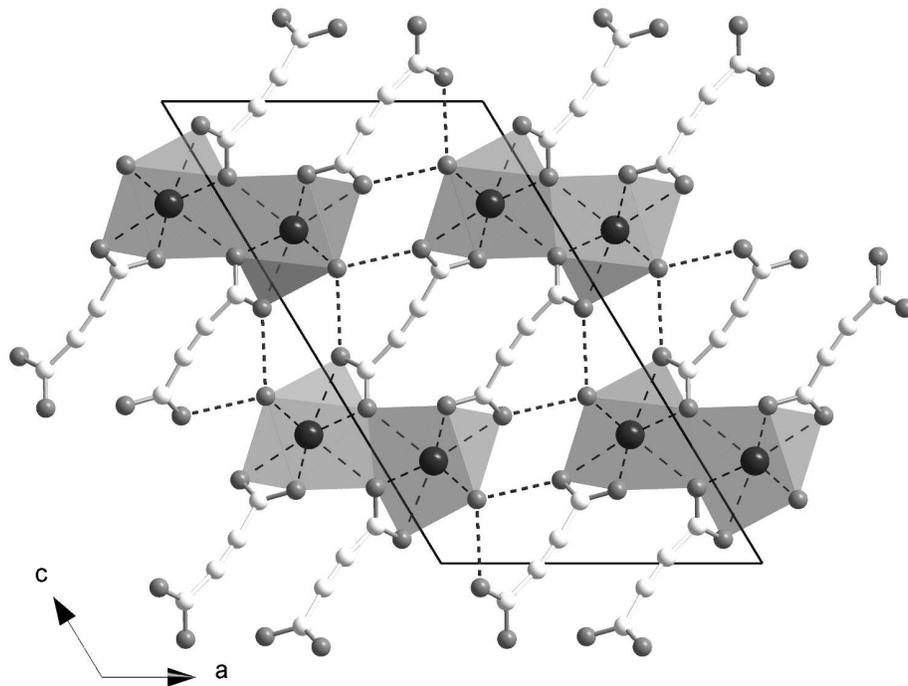
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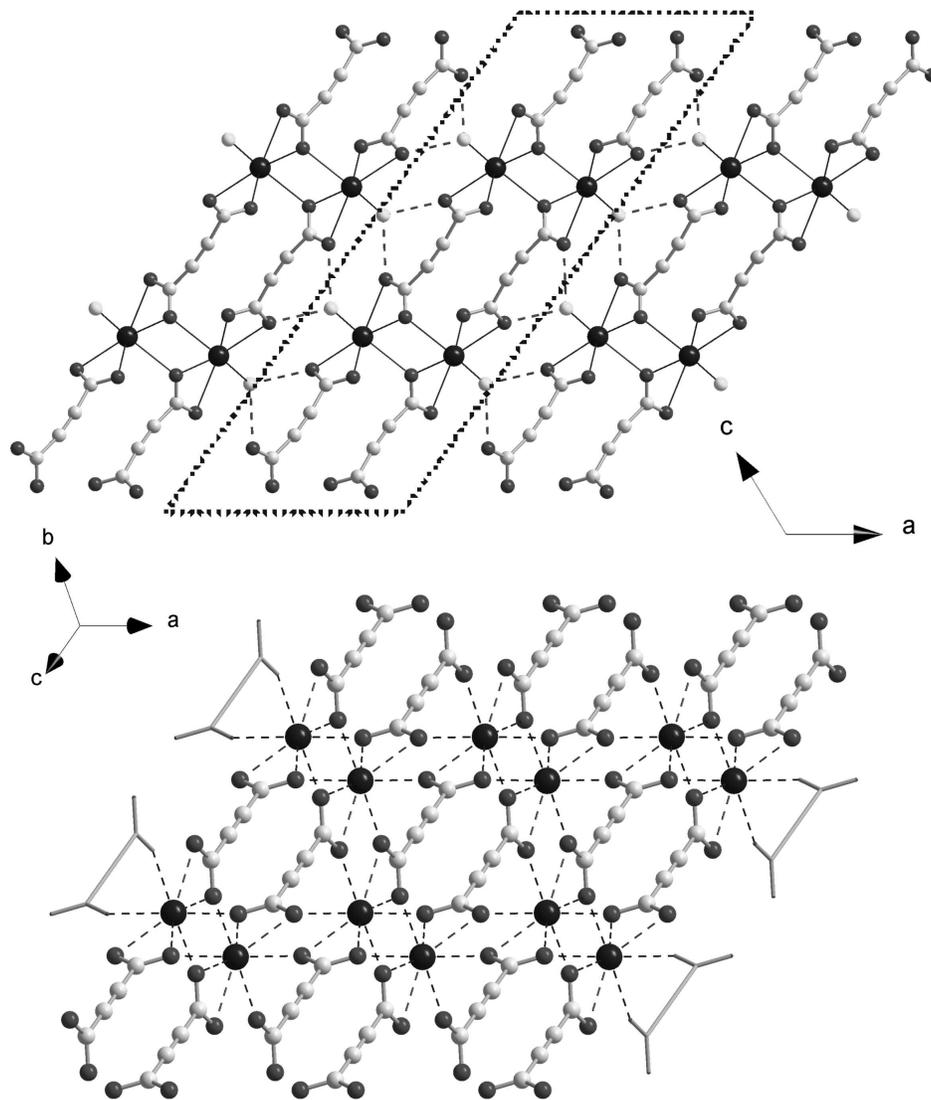
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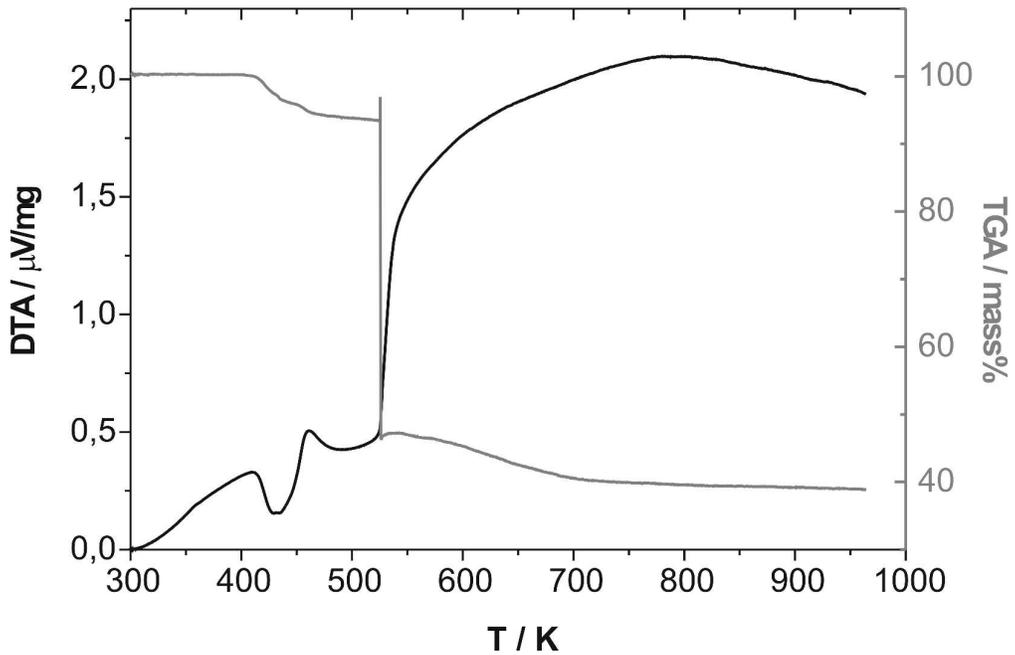




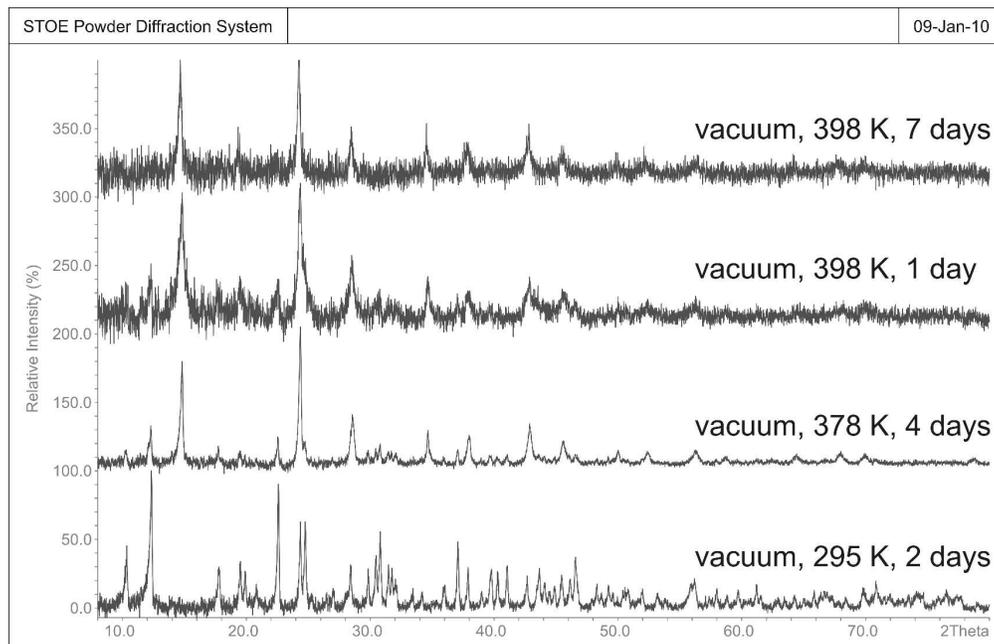


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