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**Mechanochemical synthesis of new coordination polymers with
acetylenedicarboxylate as bridging ligand**

Irena Stein and Uwe Ruschewitz*

Köln, Institut für Anorganische Chemie der Universität

Dedicated to Prof. Hans-Jörg Deiseroth on the occasion of his 65th birthday.

Bei der Redaktion eingegangen am

Abstract CaADC (**1**) and Mg(ADC)(H₂O)₂ (**2**) were synthesized by grinding Ca(CH₃COO)₂ and Mg(CH₃COO)₂ · 4 H₂O with acetylenedicarboxylic acid (H₂ADC) in an agate mortar. After careful heating for two hours in an argon atmosphere at moderate temperatures – 50°C and 70°C, resp. – polycrystalline materials of good crystallinity were obtained. The crystal structures of **1** and **2** were solved and refined from X-ray powder diffraction data. In the course of the structural refinement it turned out that **1** and **2** are isotopic to SrADC (I4₁/amd, Z = 4) and Mn(ADC)(H₂O)₂ (I2/a, Z = 4). In both compounds metal cations are connected by bridging ADC²⁻ ligands to form a 3D coordination network. Thermoanalytical investigations show that CaADC decomposes above 50°C, whereas for Mg(ADC)(H₂O)₂ a mass loss of approx. 33 % is observed above 150°C. The loss of one water molecule as well as a decarboxylation is very likely. The remaining residue is amorphous to X-rays.

Mechanochemische Synthese von neuen Koordinationspolymeren mit Acetylendicarboxylat als verbrückendem Liganden

Inhaltsübersicht Durch Verreiben von Ca(CH₃COO)₂ bzw. Mg(CH₃COO)₂ · 4 H₂O mit Acetylendicarbonsäure (H₂ADC) in einem Achatmörser wurden CaADC (**1**) und Mg(ADC)(H₂O)₂ (**2**) dargestellt. Nach Heizen bei 50°C bzw. 70°C für zwei Stunden in einer Argon-Atmosphäre konnte ein polykristallines Pulver guter Kristallinität erhalten werden. Die Kristallstrukturen von **1** und **2** wurden gelöst und verfeinert auf Basis von Röntgenpulverbeugungsdaten. Im Laufe der Strukturverfeinerung stellte sich heraus, dass beide Verbindungen isotyp zu bereits bekannten Koordinationspolymeren des Acetylendicarboxylats sind: SrADC (I4₁/amd, Z = 4) bzw. Mn(ADC)(H₂O)₂ (I2/a, Z = 4). In beiden Verbindungen werden die Metallkationen über verbrückende ADC²⁻ - Liganden zu einem 3D-Koordinationsnetzwerk verknüpft. Thermoanalytische Untersuchungen zeigen, dass sich CaADC oberhalb 50°C kontinuierlich zersetzt, während für Mg(ADC)(H₂O)₂ oberhalb 150°C ein Massenverlust von ca. 33 % gefunden wird. Dieser deutet auf den Verlust eines Wassermoleküls sowie eine Decarboxylierung hin. Der zurückbleibende Rückstand ist röntgenamorph.

Keywords: Alkaline Earth Metal; Coordination Polymer; Crystal Structure; Mechanochemical Synthesis; X-ray Powder Diffraction

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1 Introduction

In the last years the synthesis and structural characterisation of coordination polymers has been in the focus of many research groups world-wide. This interest is based on the easy preparative accessibility of these compounds and their potential applications [1]. The latter are mainly concentrated on porous coordination polymers (PCP) or metal-organic frameworks (MOF) [2]. But also non-porous coordination polymers promise interesting properties [3]. In the last years we have mainly concentrated our work in this field on the synthesis of coordination polymers containing acetylenedicarboxylate (ADC^{2-}) as bridging ligand [4-15]. Anhydrous [4-6] as well as water containing compounds [7-12] were synthesized. Recently, we were able to incorporate additional ligands like NO_3^- [13] or N donor ligands [14, 15] in these coordination polymers.

Most coordination polymers described in the literature were synthesized by solvothermal methods. Especially for porous compounds like MOF-5 [16], MIL-53 [17] or HKUST-1 [18] it is the method of choice. However, for the synthesis of coordination polymers containing ADC^{2-} as bridging ligand solvothermal methods are not applicable, as ADC^{2-} decomposes under the conditions typically used in solvothermal syntheses. Therefore other synthesis routes like slow evaporation of the solvent, diffusion methods in an H shaped tube or gel methods were successfully applied. Recently, it was shown that mechanochemical syntheses can be used to synthesize a variety of interesting solid state compounds [19]. Among them are carbides [20] as well as coordination polymers [21-23]. It was already shown that known acetylenedicarboxylates can be reproduced by mechanochemical methods [23]. But to our knowledge, the synthesis and structural characterisation of new and unknown coordination polymers obtained via mechanochemical routes is very rare. Here we present two new coordination polymers containing ADC^{2-} as bridging ligand, which were synthesized by mechanochemical methods and whose crystal structures were solved and refined from X-ray powder diffraction data.

2 Synthesis

Polycrystalline powders of **1** and **2** were obtained by grinding acetates of the respective alkaline earth metals with acetylenedicarboxylic acid (H_2ADC) in an agate mortar. To

1
2 enhance the crystallinity of the samples, they were heated for 2 hours at modest temperatures
3
4 in an argon atmosphere. No yield was determined, but according to elemental analysis and X-
5
6 ray powder diffraction data the samples are nearly single-phase.
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9 CaADC (**1**): In an agate mortar 0.08 g (0.5 mmol) $\text{Ca}(\text{CH}_3\text{COO})_2$ and 0.06 g (0.5 mmol)
10 H_2ADC were carefully ground for several minutes. A smell of acetic acid indicated the
11 proceeding reaction. The resulting sample was heated in an argon atmosphere for two hours at
12 50°C . The crystallinity of the resulting sample had significantly improved compared to the
13 unheated sample, as indicated by much narrower reflections. According to X-ray powder
14 diffraction data the sample is single-phase. Elemental analysis: calc. for $\text{C}_4\text{O}_4\text{Ca}$ (152.12):
15 C 31.58 %; found: C 32.98 %, H 0.09 %. The small deviation in the elemental analysis might
16 indicate an unknown (amorphous) impurity or some unreacted starting material.
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24 Mg(ADC)(H_2O)₂ (**2**): In an agate mortar 0.11 g (0.5 mmol) $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 0.06
25 g (0.5 mmol) H_2ADC were carefully ground for several minutes. A smell of acetic acid
26 indicated the proceeding reaction. The resulting sample was heated in an argon atmosphere
27 for two hours at 70°C . The crystallinity of the resulting sample had significantly improved
28 compared to the unheated sample, as indicated by much narrower reflections. According to X-
29 ray powder diffraction data and elemental analysis the sample is single-phase. Elemental
30 analysis: calc. for $\text{C}_4\text{H}_4\text{O}_6\text{Mg}$ (172.37): C 27.87 %, H 2.34 %; found: C 28.07 %, H 1.91
31 %.
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43 **3 Crystal Structures**

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45 Polycrystalline powders of reasonable crystallinity (see Figure 1) were obtained by
46 mechanochemical synthesis and subsequent heating at very modest temperatures as described
47 above. Samples were sealed in glass capillaries (\varnothing 0.3 mm) in an argon atmosphere. Powder
48 diffraction data were collected on a Stoe STADI P X-ray powder diffractometer ($T \approx 295\text{ K}$,
49 $\text{CuK}\alpha_1$ radiation, Ge monochromator, linear PSD detector). The collection time for one data
50 set was approx. 48 hours with steps $\Delta 2\theta = 0.01^\circ$. More details of the measurements are given
51 in Table 1.
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59 < Table 1 >

60 < Figure 1 >

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2 The diffraction data were analysed using the WinXPOW software package [24]. The
3
4 diffraction data of CaADC (**1**) were indexed in a tetragonal unit cell ($a \approx 688$ pm, $c \approx 1020$
5
6 pm) using TREOR [25]. The reflection conditions led to $I4_1/amd$ (no. 141) as possible space
7
8 group. At this point it was already speculated that CaADC is isotypic to SrADC ($I4_1/amd$, $a \approx$
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10 721 pm, $c \approx 1034$ pm) [4]. A comparison of the diffraction data of **1** with those of SrADC
11
12 confirmed this assumption. Using the atomic parameters of SrADC as starting parameters the
13
14 diffraction data of **1** were successfully refined using GSAS [26]. Bond soft constraints were
15
16 used within the ADC^{2-} anion (C1 – C1: 120 pm, C1 – C2: 147 pm, C2 – O: 125 pm). More
17
18 details of the structural refinement are given in Table 1 [27]. Selected interatomic distances
19
20 and bond angles are listed in Table 2.

21 < Table 2 >

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23 As already mentioned, CaADC (**1**) crystallizes in the SrADC type structure [4]. The carbon
24
25 backbone of the ADC^{2-} dianion is aligned along the c axis of the tetragonal unit cell with the
26
27 two carboxylate groups being perpendicular to each other (point group $\bar{4}2m$). The bond
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29 distances within the anion are constrained, but the resulting bond angles are as expected (see
30
31 Table 2). Each Ca^{2+} cation is surrounded by eight oxygen atoms of six different carboxylate
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33 ligands (Figure 2) with two of them coordinating in a chelating-type bidentate mode (Ca–O:
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35 272.8 pm, 4 x) and four in a unidentate mode (Ca–O: 231.56 pm, 4 x). Each oxygen atom of
36
37 the carboxylate groups is involved in both a bidentate and a unidentate coordination and
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39 bridges two calcium atoms in a way that a three dimensional framework results.

40 < Figure 2 >

41
42 The Ca^{2+} cations display an almost undistorted diamond-like arrangement, as can be seen in
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44 Figure 3. Each Ca^{2+} is surrounded by four other metal ions (428.1 pm, 4 x), the resulting
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46 tetrahedron is only slightly distorted (Ca – Ca – Ca: 106.9° , 2 x and 110.8° , 4 x). This close
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48 relationship to the diamond structure is also reflected in the unit cell ($c \approx \sqrt{2} \cdot a$) and space
49
50 group of **1**, as $I4_1/amd$ is a direct subgroup of $Fd\bar{3}m$, the space group of the diamond
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52 structure.

53 < Figure 3 >

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55 The diffraction data of $Mg(ADC)(H_2O)_2$ (**2**) were indexed in a monoclinic unit cell using ITO
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57 [28]. The reflection conditions led to Ia (no. 9) and $I2/a$ (no. 15) as possible space groups. The
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59 crystal structure of **2** was solved in space group $I2/a$ using EXPO2004 [29]. Only after
60
structural solution it became clear that **2** is isotypic to known compounds of composition

1
2 $M^{II}(ADC)(H_2O)_2$ with $M^{II} = Mn$ [30], Co [7], Ni [9]. The latter were described in $C2/c$. As the
3 monoclinic angle β is larger than 120° using this cell choice, it was abandoned to transform
4 the structural data of **2** from $I2/a$ to $C2/c$. The structural refinement was performed with
5 GSAS [26]. Bond soft constraints ($C1 - C1$: 120 pm, $C1 - C2$: 147 pm, $C2 - O$: 125 pm) and
6 bond angle soft constraints ($O1 - C2 - O2$: 124° , $O1 - C2 - C1$: 118° , $O2 - C2 - C1$: 118°)
7 were applied within the ADC^{2-} anion. More details of the structural refinement are given in
8 Table 1 [27]. Selected interatomic distances and bond angles are listed in Table 2.
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15 < Figure 4 >
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17 As already mentioned $Mg(ADC)(H_2O)_2$ (**2**) crystallizes in the $Mn(ADC)(H_2O)_2$ type structure
18 [30]. The coordination sphere around a Mg^{2+} cation is shown in Figure 4. Mg^{2+} is coordinated
19 octahedrally by six oxygen atoms stemming from four different carboxylate ligands ($Mg - O$:
20 205.2 pm, 2x; 217.1 pm, 2x) and two water molecules ($Mg - O$: 213.8 pm, 2x). Each oxygen
21 atom of the carboxylate groups is coordinated in a unidentate mode to just one Mg^{2+} cation.
22 These cations are connected by the ligands to form a three dimensional framework. This is
23 shown in a projection along $[010]$ in Figure 5. The carboxylate groups of the ADC^{2-} ligand
24 are almost perpendicular to each other. The angle between the planes formed by the
25 carboxylate groups is 98.14° .
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34 < Figure 5 >
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41 **4 Thermoanalytical Investigations**

42 To check the thermal stability of $CaADC$ (**1**) and $Mg(ADC)(H_2O)_2$ (**2**), DTA/TG
43 investigations were performed on both compounds in the temperature range $20^\circ C - 300^\circ C$
44 with a heating rate of $5^\circ C/min$ in an inert argon atmosphere (Netzsch STA 409C/CD, Al_2O_3
45 container). The results on $CaADC$ are shown in Figure 6. It is obvious that **1** decomposes at
46 very modest temperatures starting at approx. $50^\circ C$, the temperature at which the sample was
47 heated to improve its crystallinity. The decomposition occurs continuously as indicated by a
48 permanent mass loss. A very broad signal in the DTA curve at approx. $150^\circ C$ cannot be
49 interpreted. The low thermal stability of $CaADC$ compared to isotypic $SrADC$, which
50 decomposes above 700 K [4], is surprising, but no reasonable explanation can be given at the
51 moment.
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< Figure 6 >

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2 The DTA/TG curve obtained for Mg(ADC)(H₂O)₂ (**2**) is shown in Figure 7. Above 150°C a
3 mass loss of approx. 33 % (≈ 57 g/mol) accompanied by a broad endothermic DTA signal
4 followed by a sharper exothermic signal is observed. This could be indicative for a loss of one
5 water molecule (18 g/mol) followed by a decarboxylation (44 g/mol). But also the loss of two
6 water molecules (36 g/mol) followed by the release of one CO molecule (28 g/mol), as found
7 for SrADC [4], cannot be excluded at this point. The residue obtained after this thermal
8 treatment is amorphous to X-rays so that no further information was available.

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15 < Figure 7 >
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22 5 Conclusion and Outlook

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24 Two new coordination polymers were synthesized by mechanochemical synthesis involving
25 grinding of the starting materials in an agate mortar. After heating at moderate temperatures
26 crystalline samples were obtained giving X-ray powder diffraction patterns of reasonable
27 quality (Figure 1). Although both compounds are isotypic to known compounds, the crystal
28 structure of **2** was solved *ab initio*, as the isotypy to Mn(ADC)(H₂O)₂ [30] was only
29 recognized *after* the structural solution. This shows that compounds obtained by
30 mechanochemical synthesis cannot only be characterized by comparison with known
31 compounds, but also an *ab initio* structural solution of unknown compounds is possible. It
32 was also attempted to solve the crystal structure of **1** *ab initio* from powder diffraction data,
33 although the isotypy to SrADC [4] was obvious. Using EXPO2004 [29] a reasonable
34 structural model was obtained in space group I4₁/a. After transformation into space group
35 I4₁/amd a structural model very similar to the final crystal structure as given in Table 1 and
36 Figure 2 was obtained.

37
38 Especially the synthesis of CaADC (**1**) was of interest for us, as SrADC [4] and BaADC [31]
39 show a negative thermal expansion. As **1** is isotypic to the two other alkaline earth metal
40 compounds, it can be expected that negative thermal expansion also occurs in **1**. Due to the
41 low thermal stability of **1**, temperature dependent measurements below room temperature are
42 necessary, which will be recorded in the near future.

43
44 Many coordination polymers and MOFs are synthesized by solvothermal methods. But this
45 approach is not applicable for the synthesis of coordination polymers containing
46 acetylenedicarboxylate as linking ligand, as it decomposes under the conditions of a
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2 solvothermal synthesis. Therefore other syntheses like isothermal evaporation of the solvent,
3 gel methods or diffusion methods – e.g. in an H shaped tube – were successfully applied. But
4 up to now none of these methods allowed the synthesis of **1**. Thus, the mechanochemical
5 route is an ideal complementary approach for the synthesis of coordination polymers with
6 ADC²⁻.
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11 We have also tried to apply the mechanochemical route to the synthesis of coordination
12 polymers with other linker ligands. But reactions neither with 1,3,5-benzenetricarboxylic acid
13 (trimesic acid) nor 1,4-benzenedicarboxylic acid (terephthalic acid) were successful up to now
14 [32]. We assume that the strength of the respective acid compared to acetic acid ($pK_A = 4.76$),
15 if acetates are used as starting compounds, is important for a successful synthesis by grinding
16 in a mortar. The acidity of acetylenedicarboxylic acid ($pK_{A1} = 1.73$) seems to be high enough,
17 whereas trimesic acid ($pK_{A1} = 3.12$) and terephthalic acid ($pK_{A1} = 3.51$) are less acidic so that
18 no reaction occurs in a mortar. It was shown that using a high-energy ball mill also
19 coordination polymers with trimesic and terephthalic acid can be obtained [23]. But in this
20 case also other starting metal salts than acetates were used. Obviously, in a high-energy ball
21 mill the influence of different pK_A values is less pronounced. This is supported by the fact
22 that also basic linker ligands like 4,4'-bipyridine gave very good results in a ball mill [23].
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41 investigations.
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31 [27] Crystallographic data (excluding structure factors) for the structures reported in this
32 paper have been deposited with the Cambridge Crystallographic Data Centre as
33 supplementary publication no. CCDC-741331 (CaADC (1)) and CCDC-741332
34 (Mg(ADC)(H₂O)₂ (2)). Copies of the data can be obtained free of charge on
35 application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44
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Table 1 Details of crystal structural analysis of CaADC (1) and Mg(ADC)(H₂O)₂ (2).

	CaADC (1)	Mg(ADC)(H ₂ O) ₂ (2)
Formula	C ₄ O ₄ Ca	C ₄ H ₄ O ₆ Mg
Diffractometer, λ	Stoe STADI P, 154.059 pm	Stoe STADI P; 154.059 pm
Refined data range	$10^\circ \leq 2\theta \leq 80^\circ$	$10^\circ \leq 2\theta \leq 70^\circ$
Temperature/K	295(2)	295(2)
Space group; Z	I4 ₁ /amd (no. 141), 4	I2/a (no. 15), 4
Unit cell	a = 687.78(3) pm b = a c = 1020.11(4) pm $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$	a = 1120.22(6) pm b = 721.33(3) pm c = 761.56(4) pm $\alpha = 90^\circ$ $\beta = 92.667(3)^\circ$ $\gamma = 90^\circ$
Volume	0.48255(5) nm ³	0.61471(6) nm ³
Density calculated	2.094 kg/dm ³	1.819 kg/dm ³
No. of refined reflections	46	133
No. of refined parameters	47 (incl. 28 BG parameters)	51 (incl. 24 BG parameters)
R _P ; wR _P ; R _{Bragg}	0.0183; 0.0271; 0.0196	0.0328; 0.0460; 0.1035
$\Delta\rho_{\min/\max}$ /pm ⁻³	-0.16·10 ⁻⁶ / 0.24·10 ⁻⁶	-0.53·10 ⁻⁶ / 0.56·10 ⁻⁶

Table 2 Selected interatomic distances (pm) and angles (°) in CaADC (1) and Mg(ADC)(H₂O)₂ (2).

CaADC (1)				Mg(ADC)(H ₂ O) ₂ (2)			
Ca	- O	231.56 (9)	4 x	Mg	- O2	205.2 (3)	2x
	- O	272.8 (2)	4 x		- O3	213.8 (4)	2x
					- O1	217.1 (3)	2x
C1	- C1	120 ¹		C1	- C1	120 ¹	
C1	- C2	147 ¹		C1	- C2	147 ¹	
C2	- O	125 ¹	2x	C2	- O1	125 ¹	
				C2	- O2	125 ¹	
C1	- C1 - C2	180		C1	- C1 - C2	175 (1)	
O	- C2 - O	128.3 (2)		O1	- C2 - O2	124.0 ¹	
O	- C2 - C1	115.86 (8)	2x	O1	- C2 - C1	118.0 ¹	
				O2	- C2 - C1	118.0 ¹	

¹ soft constraints

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3 **Figure captions**
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7 **Fig. 1** X-ray powder diffraction data of CaADC (black) and Mg(ADC)(H₂O)₂ (grey),
8 collected on a Stoe STADI P diffractometer (CuK α ₁ radiation).
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13 **Fig. 2** CaADC (**1**): Coordination sphere around Ca showing the atom-numbering scheme.
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18 **Fig. 3** CaADC (**1**): Sketch of the crystal structure emphasizing the diamond-like arrangement
19 of Ca²⁺ cations; for clarity only two ADC²⁻ ligands are viewed. Ca: large dark spheres, O:
20 small grey spheres, C: small white spheres.
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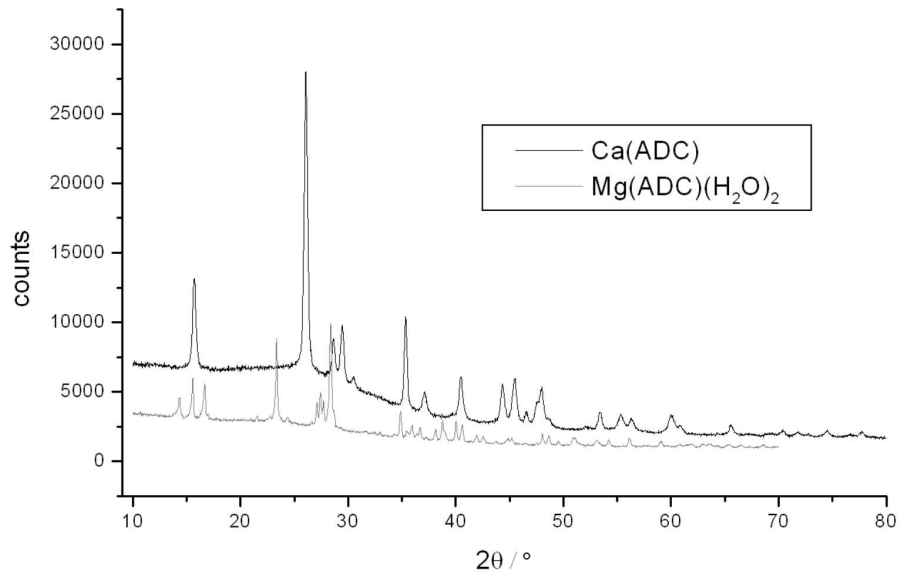
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26 **Fig. 4** Mg(ADC)(H₂O)₂ (**2**): Coordination sphere around Mg showing the atom-numbering
27 scheme. No hydrogen atoms have been refined for water molecule O3.
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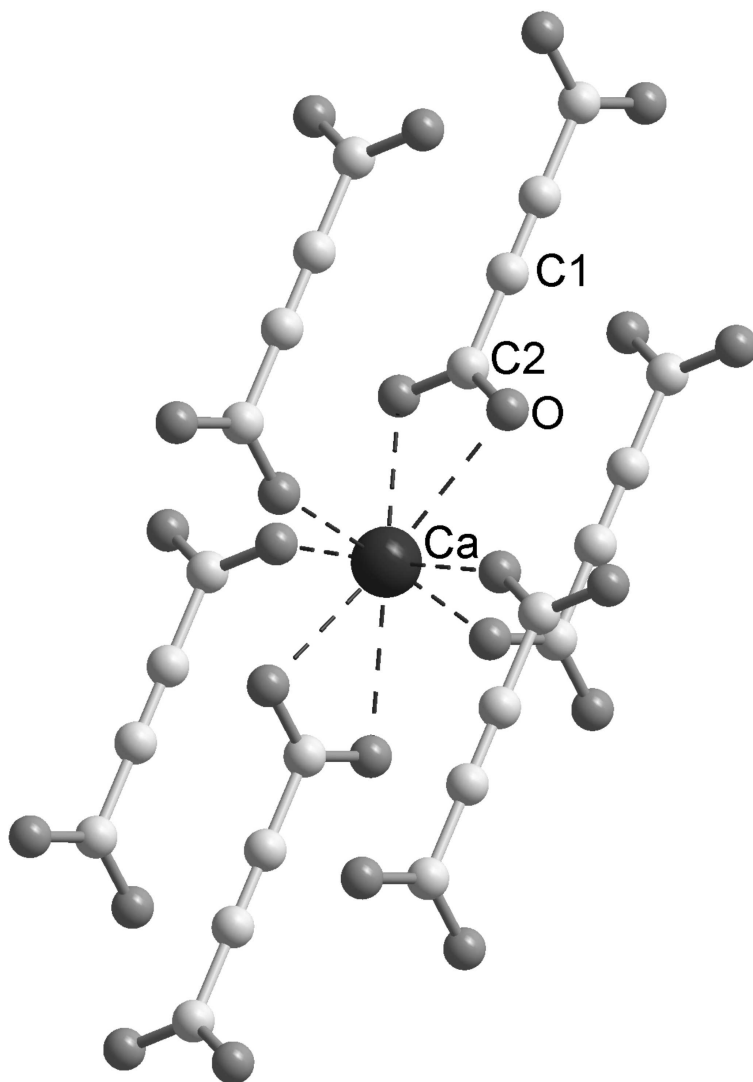
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33 **Fig. 5** Mg(ADC)(H₂O)₂ (**2**): Sketch of the crystal structure in a projection along [010]. Mg:
34 large dark spheres, O: small grey spheres, C: small white spheres.
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39 **Fig. 6** CaADC (**1**): DTA (black) and TG (grey) curves.
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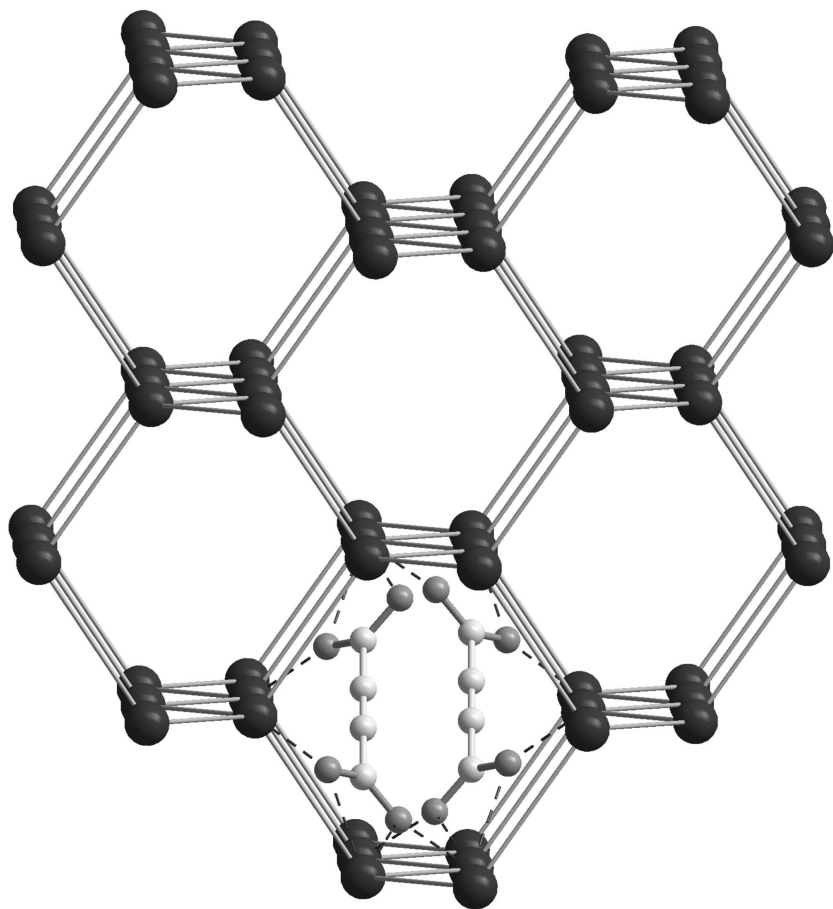
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43 **Fig. 7** Mg(ADC)(H₂O)₂ (**2**): DTA (black) and TG (grey) curves.
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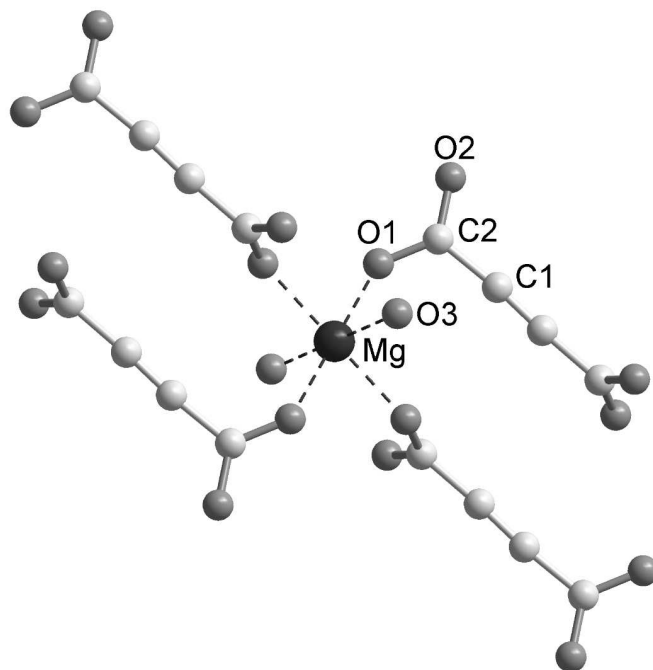
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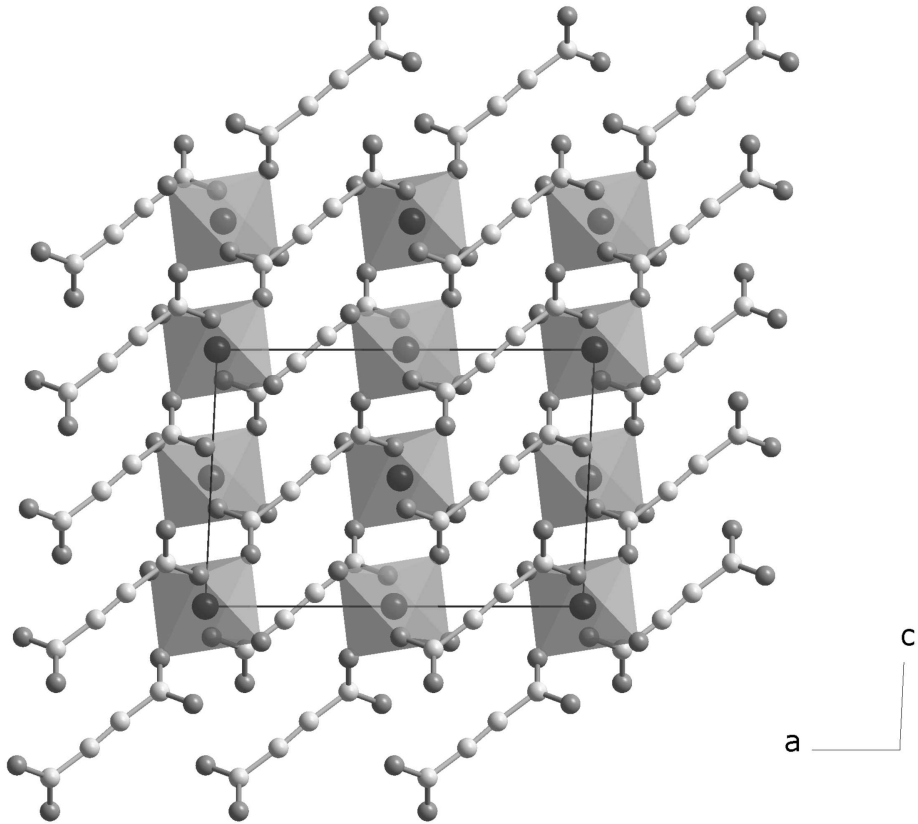


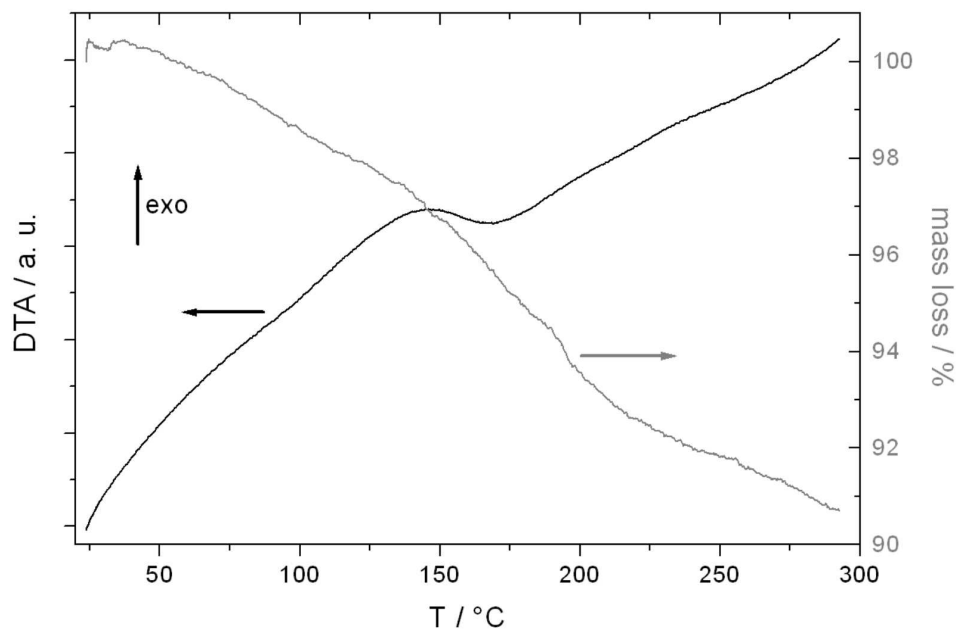
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