

# Sr[C<sub>2</sub>(COO)<sub>2</sub>]: The First Anhydrous Salt of Acetylenedicarboxylic Acid

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*Dedicated to Prof. Dr. Dieter Naumann on the occasion of his 60th birthday*

**Abstract:** Single crystals of Sr[C<sub>2</sub>(COO)<sub>2</sub>] were formed at the phase boundary of an aqueous silica gel that contained acetylenedicarboxylic acid and an aqueous solution of SrCl<sub>2</sub>. The crystal structure (*I*<sub>4</sub><sub>1</sub>/*amd*, *Z* = 4) shows a diamond-like topology, with the strontium ions in an eightfold co-ordination by the oxygen atoms of six carboxylate ligands with two of them co-ordinating in a chelating-type bidentate mode. As each oxygen atom of the carboxylate groups is involved in both a chelating-type bidentate and unidentate co-ordi-

nation and, therefore, bridging two strontium atoms, a three-dimensional framework results. Sr[C<sub>2</sub>(COO)<sub>2</sub>] exhibits a surprising thermal stability. In air decomposition starts at about 720 K and in an argon atmosphere around 750 K. This decomposition is accompanied by a mass loss of approximately 12%, which

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is probably due to the loss of one CO molecule. The resulting residue is amorphous to X-rays. A small negative thermal expansion is found between 30 and 280 K, whereas between room temperature and 573 K almost no thermal expansion is observed. Single-crystal investigations at different temperatures show a strong “guitar string” vibration of the oxygen atom perpendicular to the contacts to the strontium atoms; this could be responsible for the thermal expansion behaviour.

## Introduction

The design of new solid-state architectures consisting of metal ions and polydentate organic ligands has received much attention in the last years.<sup>[1]</sup> The interest is mainly driven by two aspects: the crystal engineering of co-ordination polymers, with the aim to gain control of the topology and geometry of the frameworks formed,<sup>[2]</sup> and the synthesis of porous materials as zeolite analogues.<sup>[3]</sup> In both cases the co-ordination geometry of the metal, which is a transition or rare-earth metal in most cases, and the structure of the polydentate ligand are essential for the desired tuning of the properties of inorganic–organic frameworks. Therefore ligands with a rigid carbon backbone are preferred. In this respect we have started to investigate possible co-ordination polymers of the acetylenedicarboxylate dianion (C<sub>2</sub>(COO)<sub>2</sub><sup>2−</sup> = ADC<sup>2−</sup>),<sup>[4]</sup> which has not received too much interest up to now.

To the best of our knowledge—besides some salts of the hydrogen acetylenedicarboxylate anion (HADC<sup>−</sup>)<sup>[5–11]</sup>—only BeADC · 4H<sub>2</sub>O,<sup>[12]</sup> MnADC · 2H<sub>2</sub>O,<sup>[13]</sup> BaADC · H<sub>2</sub>O<sup>[14]</sup> and very recently Zn(ADC)<sub>2</sub> · (HTEA)<sub>2</sub>,<sup>[15]</sup> which contains disor-

dered ADC<sup>2−</sup> ligands and disordered triethylammonium cations (HTEA<sup>+</sup>) in the cavities of the Zn–ADC framework, are known and have been structurally characterised. BeADC · 4H<sub>2</sub>O consists of Be(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> tetrahedra and ADC<sup>2−</sup> anions linked to a three-dimensional framework. In MnADC · 2H<sub>2</sub>O the manganese cation is octahedrally co-ordinated by four oxygen atoms of the ADC<sup>2−</sup> ligands and two water molecules to form a three-dimensional framework. A three-dimensional framework is also formed in BaADC · H<sub>2</sub>O, but the barium cation is co-ordinated by seven oxygen atoms of the ADC<sup>2−</sup> ligands and two water molecules. Furthermore information on the thermal properties of hydrated transition metal acetylenedicarboxylates is available based on TG/DTA measurements.<sup>[16–18]</sup>

Here we report on the synthesis and crystal structure of Sr[C<sub>2</sub>(COO)<sub>2</sub>] (**1**), the first anhydrous salt of the acetylenedicarboxylate dianion, which shows a surprising thermal stability up to 750 K and a small negative thermal expansion between 30 K and 280 K.

## Results and Discussion

Sr[C<sub>2</sub>(COO)<sub>2</sub>] (**1**, C<sub>2</sub>(COO)<sub>2</sub><sup>2−</sup> = acetylenedicarboxylate dianion) was synthesised from an aqueous silica gel that contained acetylenedicarboxylic acid (see Experimental Sec-

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tion) layered with an aqueous solution of  $\text{SrCl}_2$ . Single crystals of **1** formed at the phase boundary. After washing with ethanol and diethyl ether a single-phase product was obtained as checked by X-ray powder diffraction and elemental analysis. The resulting colourless powder and the single crystals are stable to air and moisture and can be stored without any further precautions. No melting was observed up to 643 K. The Raman spectrum of **1** shows a strong signal at  $2230\text{ cm}^{-1}$ , which can be attributed to the  $\text{C}\equiv\text{C}$  stretching vibration, and two signals at  $1598$  and  $1415\text{ cm}^{-1}$  for the antisymmetric and symmetric stretching vibrations of the carboxylate group. For pure  $\text{C}_2(\text{COOH})_2$  two signals for the  $\text{C}\equiv\text{C}$  stretching vibration were found at  $2272$  and  $2241\text{ cm}^{-1}$ . Thus, the respective frequency of **1** is slightly shifted to lower values. This is agreement with the results obtained for  $\text{CoADC}(\text{H}_2\text{O})_2$  ( $\tilde{\nu} = 2232\text{ cm}^{-1}$ ).<sup>[19]</sup>

The crystal structure of **1** was determined by X-ray single-crystal structure analysis at three different temperatures (170 K, 293 K, 593 K; see Experimental Section). Details of the structural investigations are given in Tables 1 and 2; selected interatomic distances and angles are listed in Table 3.

**Abstract in German:** *An der Phasengrenze einer Acetylen-dicarbonsäure enthaltenden wäßrigen Silicagel-Lösung und einer wäßrigen  $\text{SrCl}_2$ -Lösung konnten Einkristalle von  $\text{Sr}[\text{C}_2(\text{COO})_2]$  erhalten werden. Die Kristallstruktur ( $I4_1/amd$ ,  $Z=4$ ) zeigt eine diamantartige Topologie, wobei die Strontiumionen achtfach von den Sauerstoffatomen von sechs Carboxylatliganden koordiniert sind, zwei von ihnen in einer chelatartigen zweizähligen Anordnung. Da wiederum jedes Sauerstoffatom der Carboxylatgruppen sowohl an einer zweizähligen chelatartigen als auch an einer einzähligen Koordination beteiligt ist und somit zwei Strontiumionen verknüpft, resultiert eine dreidimensionale Gerüststruktur.  $\text{Sr}[\text{C}_2(\text{COO})_2]$  zeigt eine überraschende thermische Stabilität. An Luft wird erst ab ca.  $720\text{ K}$  eine Zersetzung beobachtet und in einer Argonatmosphäre oberhalb von  $750\text{ K}$ . Diese Zersetzung wird von einem Massenverlust von ca.  $12\%$  begleitet, der höchstwahrscheinlich auf den Verlust eines  $\text{CO}$  Moleküls zurückzuführen ist. Der resultierende Rückstand ist röntgenamorph. Zwischen  $30$  und  $280\text{ K}$  wird eine kleine negative thermische Ausdehnung beobachtet, während oberhalb von Raumtemperatur bis ca.  $573\text{ K}$  praktisch keine thermische Ausdehnung auftritt. Einkristalluntersuchungen bei verschiedenen Temperaturen zeigen eine starke "Gitarrensaiten"-Schwingung des Sauerstoffatoms senkrecht zur Verknüpfung zweier Strontiumionen. Diese könnte für das ungewöhnliche thermische Ausdehnungsverhalten von  $\text{Sr}[\text{C}_2(\text{COO})_2]$  verantwortlich sein.*

Table 1. Details of the single-crystal X-ray investigations on  $\text{Sr}[\text{C}_2(\text{COO})_2]$ .

	170 K	293 K	593 K
space group	$I4_1/amd$ (No. 141)	$I4_1/amd$ (No. 141)	$I4_1/amd$ (No. 141)
$Z$	4	4	4
$a$ [pm]	721.8(1)	721.0(1)	720.5(1)
$c$ [pm]	1035.6(2)	1033.8(2)	1036.9(2)
$V$ [nm <sup>3</sup> ]	0.5396(2)	0.5375(1)	0.5382(2)
$\rho_{\text{calc}}$ [kg dm <sup>-3</sup> ]	2.458	2.468	2.464
$2\theta$ range [°]	6.88–55.68	6.88–57.76	6.88–56.00
index range	$-8 \leq h \leq 8$ $-9 \leq k \leq 9$ $-12 \leq l \leq 13$	$-11 \leq h \leq 11$ $-11 \leq k \leq 10$ $-16 \leq l \leq 16$	$-9 \leq h \leq 9$ $-8 \leq k \leq 8$ $-13 \leq l \leq 13$
measured reflections	2418	4614	2416
unique reflections	192	203	194
observed reflections [ $I_0 > 2\sigma(I)$ ]	160	168	158
$R_{\text{int}}$	0.0512	0.0648	0.0602
parameters	18	18	17
$R1/wR2$ [ $I_0 > 2\sigma(I)$ ]	0.0208/0.0458	0.0124/0.0284	0.0255/0.0475
$R1/wR2$ (all data)	0.0289/0.0467	0.0235/0.0304	0.0398/0.0499
$\Delta\rho_{\text{min/max}}$ [ $\times 10^{-6}\text{ pm}^{-3}$ ]	−1.094/0.570	−0.278/0.224	−0.804/0.504

Table 2. Atomic co-ordinates and equivalent isotropic displacement parameters [pm<sup>2</sup>] of  $\text{Sr}[\text{C}_2(\text{COO})_2]$ .

	170 K	293 K	593 K
Sr on 4b			
$U_{\text{eq}}$	86(3)	158(2)	275(3)
O on 16 h			
$x$	0.1534(4)	0.1524(2)	0.1512(4)
$z$	0.1310(3)	0.1311(2)	0.1302(4)
$U_{\text{eq}}$	178(6)	317(4)	507(9)
C(1) on 8e			
$z$	−0.0677(5)	−0.0673(3)	−0.0681(6)
$U_{\text{eq}}$	155(10)	255(7)	420(20)
C(2) on 8e			
$z$	0.0749(5)	0.0742(3)	0.0735(5)
$U_{\text{eq}}$	132(10)	206(6)	332(13)

Table 3. Selected interatomic distances [pm] and angles [°] of  $\text{Sr}[\text{C}_2(\text{COO})_2]$ .

	170 K	293 K	593 K
Sr–Sr	444.16(5) $4 \times$	443.58(5) $4 \times$	443.80(6) $4 \times$
Sr–O	250.2(3) $4 \times$ 275.9(3) $4 \times$	250.7(2) $4 \times$ 275.1(2) $4 \times$	251.3(3) $4 \times$ 276.3(4) $4 \times$
C(1)–C(1)	118.7(11)	119.2(6)	118.0(12)
C(1)–C(2)	147.7(7)	146.3(4)	146.8(8)
C(2)–O	125.0(3) $2 \times$	124.6(2) $2 \times$	123.8(4) $2 \times$
C(1)–C(1)–C(2)	180.0	180.0	180.0
O–C(2)–O	124.7(5)	123.7(3)	123.3(6)
O–C(2)–C(1)	117.7(2) $2 \times$	118.15(15) $2 \times$	118.3(3) $2 \times$
Sr–O–Sr	115.08(11)	114.99(7)	114.45(14)

From these tables the high quality of the crystal structure analyses is evident.

The resulting crystal structure of **1**—as obtained from the structure analysis at room temperature—viewed along the body diagonal of the tetragonal unit cell is depicted in Figure 1.

The carbon backbone of the  $\text{ADC}^{2-}$  dianion is aligned along the  $c$  axis of the tetragonal unit cell with the two carboxylate groups being perpendicular to each other. The bond distances and angles in the anion are as expected (see

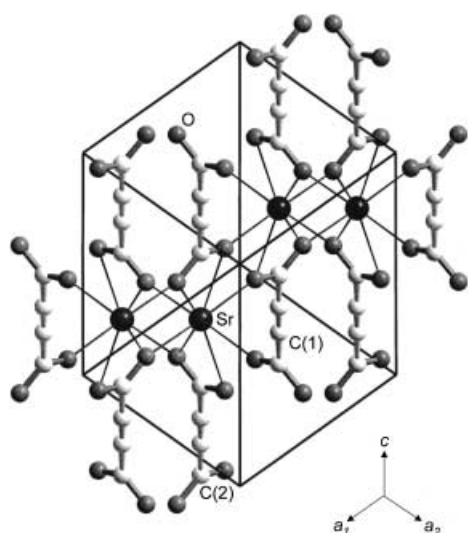


Figure 1. Crystal structure of  $\text{Sr}[\text{C}_2(\text{COO})_2]$  (293 K) in a view along  $[111]$ . Short Sr–O contacts are drawn as thin lines.

Table 3). Each  $\text{Sr}^{2+}$  is surrounded by eight oxygen atoms of six carboxylate ligands with two of them co-ordinating in a chelating-type bidentate mode (Sr–O: 275.1(2) pm) and four in a unidentate mode (Sr–O: 250.7(2) pm). As each oxygen atom of the carboxylate groups is involved in both a bidentate and a unidentate co-ordination and, therefore, bridges two strontium atoms, a three-dimensional framework results. The co-ordination around one strontium ion is depicted in Figure 2

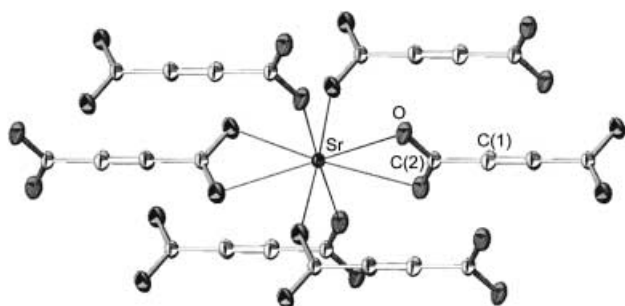


Figure 2. Co-ordination sphere around one strontium atom. Thermal ellipsoids are drawn on a 50% probability scale (293 K).

in a representation showing the thermal ellipsoids on a 50% probability scale. With the exception of  $U_{22}$  of the oxygen atom, which is slightly larger and will be discussed in another context later-on, these ellipsoids show the expected behaviour.

The  $\text{Sr}^{2+}$  cations display an almost undistorted diamond-like arrangement, as can be seen in Figure 3. Each  $\text{Sr}^{2+}$  is surrounded by four  $\text{Sr}^{2+}$  ( $\text{Sr} \cdots \text{Sr} = 443.58(5)$  pm), the resulting tetrahedron is only slightly distorted (Sr–Sr–Sr:  $108.73^\circ$  ( $2 \times$ ) and  $109.84^\circ$  ( $4 \times$ )). This close relationship to the diamond structure is also reflected in the unit cell ( $c \sim \sqrt{2}a$ ) and space group of **1**;  $I4_1/amd$  is a direct subgroup of  $Fd\bar{3}m$ , the space group of the diamond structure. To check for possible phase transitions a single-crystal analysis of **1** was also performed at 170 K and 593 K, but no deviation from the

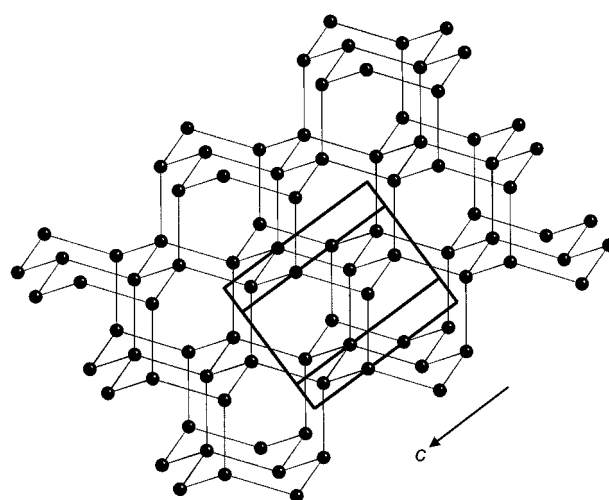


Figure 3. Diamond-like arrangement of the strontium atoms in  $\text{Sr}[\text{C}_2(\text{COO})_2]$ . The unit cell and the shortest Sr–Sr contacts are drawn.

tetragonal symmetry was found. The results of these investigations are also summarised in Table 1–3.

A surprising result given in Table 1 is that of the volumes of the unit cells obtained at different temperatures. The smallest volume is found in the room temperature investigation, the highest at low temperatures. This could be indicative for a negative thermal expansion in **1**, as found in a few other open framework materials.<sup>[20]</sup> However, as lattice parameters obtained from single-crystal diffraction data are not as reliable as those obtained from powder diffraction data we performed additional experiments at low temperatures using a high-resolution X-ray laboratory instrument, and at temperatures above room temperature we used the powder diffractometer at beamline B2 of the Hamburg synchrotron facility HASYLAB with a new position-sensitive image plate detector system, this leads to medium-resolution data (see Experimental Section). For both investigations it was found that there is almost no shift of the diffraction angles in dependence of the temperature. A strong overlap of most of the reflections is found as  $c \sim \sqrt{2}a$ , which makes the analysis of the data more difficult, but the first reflection of the pattern (101) does not coincide. For the low-temperature data it shifts from  $2\theta = 15.020(1)^\circ$  at 280 K to  $14.999(1)^\circ$  at 30 K, thus indicating a small negative expansion. This is in agreement with the results of Rietveld refinements of the different patterns, which gave more reliable lattice parameters as those obtained from a single-peak fitting procedure because of the strong reflection overlap. The cell volumes obtained from the Rietveld refinements at different temperatures are shown in Figure 4; these results confirm a small negative thermal expansion between 280 and 30 K. From these data the thermal expansion coefficient can be calculated to  $\alpha_V = -4.7(13) \times 10^{-6} \text{ K}^{-1}$ . This value is much smaller than the coefficients obtained for other negative thermal expansion materials like  $\text{ZrW}_2\text{O}_8$  ( $\alpha_V = -27.2 \times 10^{-6} \text{ K}^{-1}$  (0–300 K))<sup>[21]</sup> and  $\text{ZrV}_2\text{O}_7$  ( $\alpha_V = -21.3 \times 10^{-6} \text{ K}^{-1}$  (400–500 K))<sup>[20]</sup> and almost in the range of the standard deviation.

At temperatures from 293–573 K, even with the better resolution of the synchrotron data, no evident trend for the

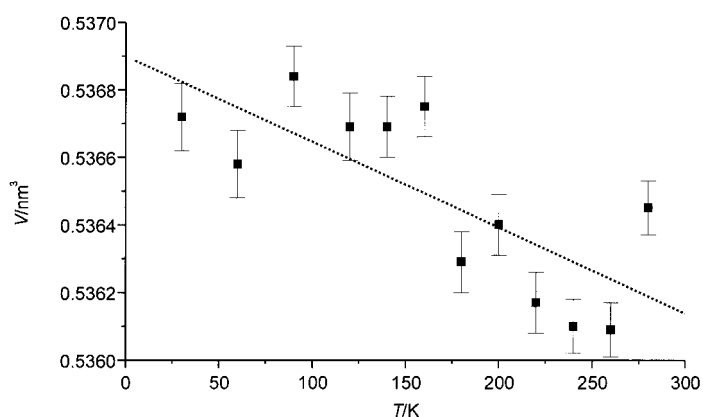


Figure 4. Volume of the unit cell of Sr[C<sub>2</sub>(COO)<sub>2</sub>] between 280 and 30 K as obtained from Rietveld refinements of the X-ray powder diffraction data.

cell volume obtained from Rietveld refinements or the diffraction angle of the (101) reflection on the dependence of the temperature was found ( $2\theta = 6.872(1)^\circ$  at 293 K and  $2\theta = 6.878(1)^\circ$  at 573 K). This effect is completely reversible, as was confirmed by data taken on cooling from 573 K to room temperature. On heating **1** to higher temperatures a small irreversible volume decrease and a colour change from white to brown indicated the start of decomposition. A confirmation for the unusual thermal expansion behaviour of **1** is the temperature dependence of the anisotropic displacement parameter  $U_{22}$  of the oxygen atom. In Figure 5 the  $U_{ii}$ 's obtained from the X-ray single-crystal analysis at three

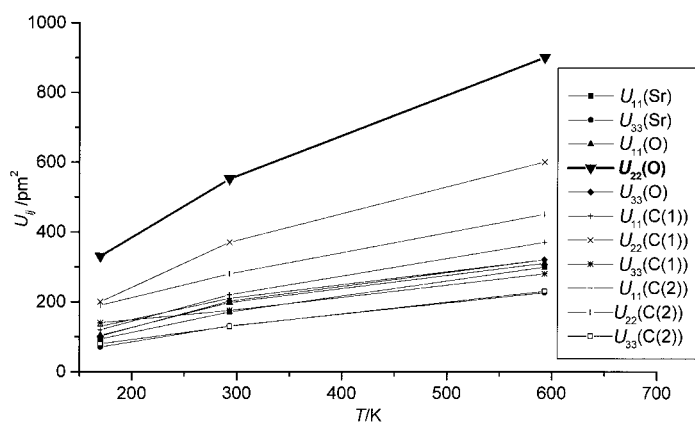


Figure 5. Anisotropic displacement parameters  $U_{ii}$  of Sr[C<sub>2</sub>(COO)<sub>2</sub>] as obtained from single-crystal X-ray analyses at different temperatures.

different temperatures are given. It is evident that the  $U_{22}$  value of the oxygen atom is distinctively higher at all temperatures than those of the other displacement parameters. This could be indicative for a strong transverse "guitar string" vibration, which was assumed to be one of the requirements for negative thermal expansion.<sup>[20]</sup> The transverse vibration of the oxygen atom connecting two strontium atoms is sketched in Figure 6.

More information on the thermal behaviour of **1** was obtained by measuring their TG/DTA curves in air and argon, respectively. The resulting diagrams without any baseline corrections are shown in Figure 7. From Figure 7a it can be

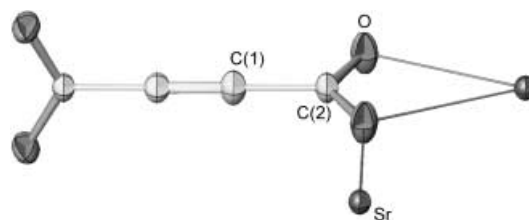


Figure 6. "Guitar string" vibration of the oxygen atoms perpendicular to the Sr–O contacts.

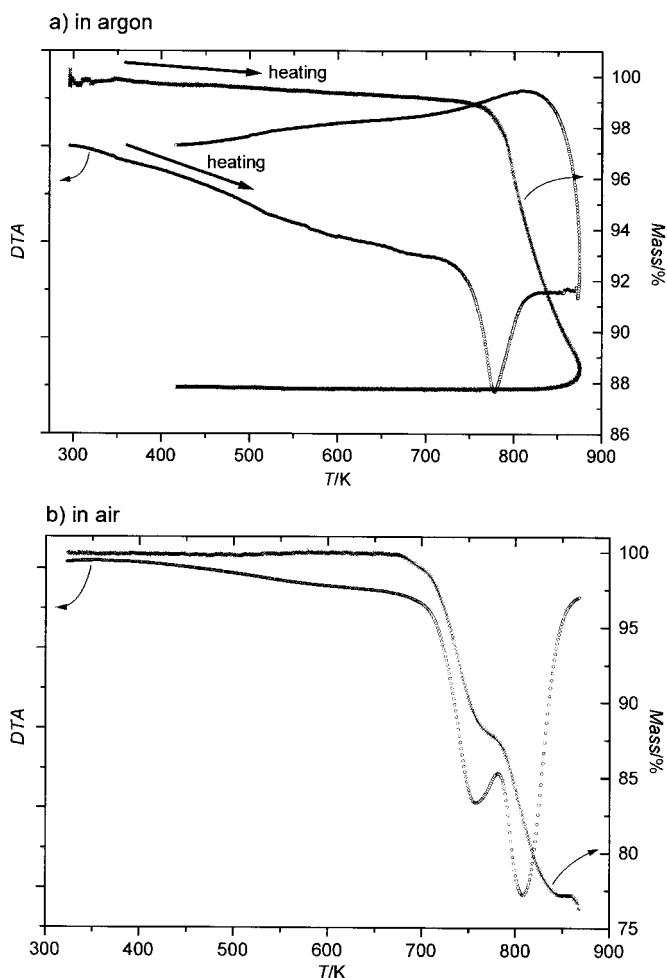


Figure 7. DTA/TG curves of Sr[C<sub>2</sub>(COO)<sub>2</sub>]. a) In argon: temperature range 293–873–416 K (heating/cooling rate: 10 K min<sup>−1</sup>); b) in air: temperature range 323–873 K (heating rate: 10 K min<sup>−1</sup>).

seen that **1** starts decomposing in argon at about 750 K, as indicated by a strong exothermic signal in the DTA curve. This is accompanied by a mass loss of about 12 %, which could point to the loss of a CO molecule (calcd: 14 %) according to Equation (1).



Unfortunately, this equation for the decomposition of **1** could not be confirmed by X-ray powder diffraction data, as the resulting black powder of the TG/DTA investigations turned out to be amorphous. The result of the TG/DTA investigation in air is shown in Figure 7b. The decomposition starts at about 720 K, only 30 K lower than the decomposition

temperature in argon. Again a mass loss of about 12 % is observed, which could be due to the loss of a CO molecule. This decomposition is followed by a second exothermic reaction at about 790 K, which is probably due to the reaction of the resulting carbon of Equation (1) with oxygen. The mass loss of approximately 11 % is close to the calculated value (12 %). The high thermal stability of **1** in argon and especially in air is surprising for a compound with a reactive C≡C triple bond. Pure C<sub>2</sub>(COOH)<sub>2</sub> already decomposes at about 450 K.

## Conclusion

Compound **1**, which can be synthesised and crystallised by a simple procedure in a two-phase aqueous system, is a compound with a surprising thermal stability up to 720 K in air. It can be speculated that this stability is caused by a close packing of the C<sub>2</sub>(COO)<sub>2</sub><sup>2-</sup> anions in the highly symmetric tetragonal crystal structure of **1**, which does not contain additional water molecules. MnADC·2H<sub>2</sub>O decomposes completely to Mn<sub>3</sub>O<sub>4</sub> after loss of its water molecules at temperatures as low as 480 K.<sup>[13]</sup> Compound **1** shows a weak negative thermal expansion between 30 and 280 K and almost no expansion between 293 and 573 K. However, the resulting effect is almost in the range of the standard deviations of the lattice parameters obtained from powder diffraction experiments at different temperatures. Therefore we are trying to grow larger crystals of **1** to perform dilatometric measurements, which should give more precise results for the thermal expansion. Furthermore we are planning to extend our syntheses to other strontium salts of dicarboxylic acids with rigid carbon backbones to see whether anhydrous compounds with similar thermal expansion properties can be obtained.

## Experimental Section

**Preparation:** Strontium acetylenedicarboxylate (**1**) was prepared by crystallisation at the phase boundary of a two-phase system. HNO<sub>3</sub> (2 M, 2 mL) was added to a solution of acetylenedicarboxylic acid (0.57 g, 5 mmol; Fluka, 99 %) in water (10 mL). A pH of approximately 5.5 was adjusted by adding an aqueous Na<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> solution ("Sodium water-glass", Fluka). This solution was layered with an aqueous SrCl<sub>2</sub> solution (1 M; SrCl<sub>2</sub>·6H<sub>2</sub>O; Fluka, ≥99 %). At the phase boundary crystals of **1** grew within a few days. They were isolated and washed with ethanol and diethyl ether. No yield was determined.

The resulting colourless solid was free of crystalline impurities, as checked by X-ray powder diffraction (see Figure 8: STOE Stadi P, Ge monochromator, Cu<sub>Kα1</sub> radiation (λ = 154.059 pm), linear position-sensitive OED detector; Rietveld refinement using GSAS software<sup>[22]</sup>). Elemental analysis calcd (%) for C<sub>4</sub>O<sub>4</sub>Sr (199.66): C 24.06; found: C 23.10.

**X-ray diffraction investigations:** A single crystal of **1** (colourless polyhedron, 0.2 × 0.2 × 0.1 mm) was isolated and sealed in a glass capillary under argon (Ø = 0.3 mm). Single-crystal X-ray data were collected on a STOE image-plate diffractometer (IPDS) by using graphite-monochromatised Mo<sub>Kα</sub> radiation (λ = 71.069 pm) at 170(2), 293(2) and 593(2) K. The structure was solved by direct methods (SIR-92)<sup>[23]</sup> and Fourier synthesis.<sup>[24]</sup> The refinement was done by full-matrix least-squares procedures using anisotropic thermal parameters (SHELXL-93).<sup>[24]</sup> Further details of the structural investigations are given in Tables 1 and 2; some selected interatomic distances and angles are listed in Table 3.

CCDC-168647 (170 K), CCDC-168648 (293 K) and CCDC-168649 (593 K) contain the supplementary crystallographic data for this paper. These data

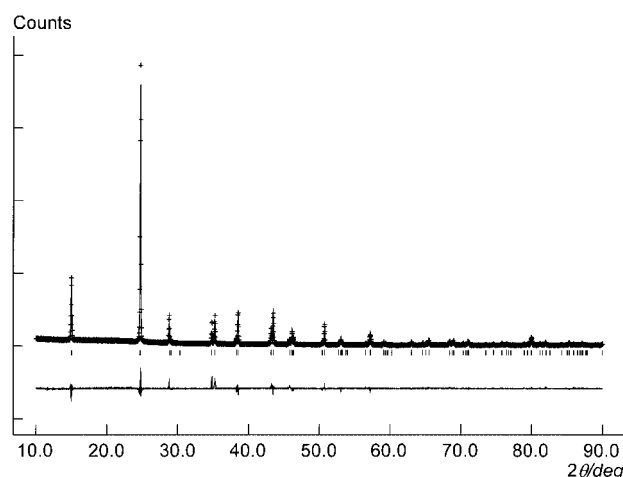


Figure 8. X-ray powder diffraction data (STOE Stadi P, Cu<sub>Kα1</sub> radiation) and Rietveld refinement of Sr[C<sub>2</sub>(COO)<sub>2</sub>] at 295 K, showing the observed (+) and calculated patterns (solid line) as well as the difference between them. Vertical bars mark the positions of the reflections.

can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

Temperature-dependent X-ray powder diffraction data at low temperatures (280–30 K) were collected on a Huber G645 Guinier camera (Ge monochromator, Cu<sub>Kα1</sub> radiation (λ = 154.059 pm), scintillation counter) equipped with a Huber closed-cycle cryostat. A thin flat sample (transmission geometry) was used for the measurement. The halfwidth of the (101) reflection was determined to 0.103° (280 K) given in 2θ.

High-temperature powder diffraction investigations (293–573 K) were carried out on the powder diffractometer at beamline B2 of the Hamburg Synchrotron facility HASYLAB (direct beam, λ = 70.8785 pm, position sensitive imaging plate detector system (OBI)<sup>[25]</sup>) equipped with a STOE furnace. The sample was sealed in a capillary (Ø = 0.3 mm) under argon for the measurement. The halfwidth of the (101) reflection was determined to 0.056° (293 K) given in 2θ.

All diffractograms were analysed using the STOE software Win XPOW.<sup>[26]</sup> For the Rietveld refinements the GSAS software package was applied.<sup>[22]</sup> To obtain a reliable trend of the lattice parameters the same sets of variables were refined in the Rietveld computations of the high and the low temperature data, respectively.

**Differential thermal analyses:** Differential thermal analyses were carried out on a Netzsch STA 409C. The measurement in argon (sample: 20.73 mg) was performed between 293 and 873 K with a heating rate of 10 K min<sup>-1</sup> and between 873 and 416 K with a cooling rate of 10 K min<sup>-1</sup>. The curve in air (sample: 14.50 mg) was measured between 323 and 873 K with a heating rate of 10 K min<sup>-1</sup>.

**Raman spectroscopy:** The Raman spectrum was recorded on a Bruker FTIR spectrometer IFS 66v/S with the Raman module Bruker FRA 106/S (Nd:YAG laser, λ = 1064 nm). The sample was sealed in a capillary under argon.

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- [1] P. J. Hargman, D. Hargman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638; A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466; *Angew. Chem. Int. Ed.* **1999**,

- 38, 3268; M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Adv. Inorg. Chem.* **1999**, *46*, 174; "Special Issue": *J. Solid State Chem.* **2000**, *152*, 1; M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.
- [2] M. J. Zaworotko, *Chem. Soc. Rev.* **1994**, *23*, 283; L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *J. Chem. Soc. Chem. Commun.* **1994**, 2755; D. M. L. Goodgame, S. Menzer, A. M. Smith, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **1997**, 3213; M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1727; S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460; S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739; A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117; B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629.
- [3] B. F. Abrahams, B. F. Hoskins, D. M. Michail, R. Robson, *Nature* **1994**, *369*, 727; S. S.-Y. Chiu, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148; H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276; J.-C. Dai, X.-T. Wu, Z.-Y. Fu, S.-M. Hu, W.-X. Du, C.-P. Cui, L.-M. Wu, H.-H. Zhang, R.-Q. Sun, *Chem. Commun.* **2002**, 12; M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 376; M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.
- [4] J. D. Dunitz, J. Monteath Robertson, *J. Chem. Soc.* **1947**, 148; V. Benghiat, L. Leiserowitz, G. M. J. Schmidt, *J. Chem. Soc. Perkin Trans. II* **1972**, 1769; A. C. Larson, D. T. Cromer, *Acta Crystallogr. Sect. B* **1973**, *29*, 1579.
- [5] I. Leban, L. Golic, J. C. Speakman, *J. Chem. Soc. Perkin Trans II* **1973**, 703.
- [6] J. Blain, J. C. Speakman, L. A. Stamp, L. Golic, I. Leban, *J. Chem. Soc. Perkin Trans. II* **1973**, 706.
- [7] I. Leban, *Cryst. Struct. Commun.* **1974**, *3*, 237.
- [8] I. Leban, *Cryst. Struct. Commun.* **1974**, *3*, 241.
- [9] M. P. Gupta, A. P. Mahata, *Cryst. Struct. Commun.* **1976**, *5*, 557.
- [10] M. P. Gupta, J. L. Agrawal, *Cryst. Struct. Commun.* **1977**, *6*, 103.
- [11] R. Mattes, G. Plescher, *Acta Crystallogr. Sect. B* **1981**, *37*, 697.
- [12] C. Robl, S. Hentschel, *Z. Naturforsch. Teil B* **1990**, *45*, 1499.
- [13] C. Robl, S. Hentschel, *Z. Anorg. Allg. Chem.* **1990**, *591*, 188.
- [14] C. Robl, S. Hentschel, *Z. Anorg. Allg. Chem.* **1991**, *596*, 149.
- [15] J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239.
- [16] J. R. Allan, P. C. Beaumont, L. Macindoe, G. H. W. Milburn, A. Werninck, *Thermochim. Acta* **1987**, *117*, 51.
- [17] W. Zamiduo, R. Baraona, *Bol. Soc. Chil. Quim.* **1994**, *39*, 339.
- [18] B. J. McCormick, C. Siemer, F. Afroz, J. R. Wasson, D. M. Eichhorn, B. Scott, S. Shah, K. Noffsinger, P. K. Kahol, *Synth. Met.* **2001**, *120*, 969.
- [19] I. Pantenburg, U. Ruschewitz, *Z. Anorg. Allg. Chem.*, **2002**, 628, 1697.
- [20] J. S. O. Evans, *J. Chem. Soc. Dalton Trans.* **1999**, 3317.
- [21] J. S. O. Evans, W. I. F. David, A. W. Sleight, *Acta Crystallogr. Sect. B* **1999**, *55*, 333.
- [22] A. C. Larson, R. B. von Dreele, *Los Alamos Natl. Lab.* **1987**, *86*, 748; revised PC version of March **2000**.
- [23] A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualardi, *J. Appl. Crystallogr.* **1993**, *26*, 343.
- [24] G. M. Sheldrick, SHELXL-93, A Program for Crystal Structure Refinement, University of Göttingen, Göttingen (Germany), **1993**.
- [25] M. Knapp, V. Joco, C. Bährt, H. H. Brecht, A. Berghäuser, H. Ehrenberg, H. von Seggern, H. Fuess, *Hasylab Jahresbericht* **2001**, 64.
- [26] Win XPOW, version 1.04, Stoe Cie, Darmstadt (Germany), **1999**.

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