DOI: 10.1002/zaac.201000245

$K_3[C_3N_3(COO)_3]\cdot 2H_2O$ – Crystal Structure of a New Alkali Derivative of the Multidentate Ligand Triazine Tricarboxylate

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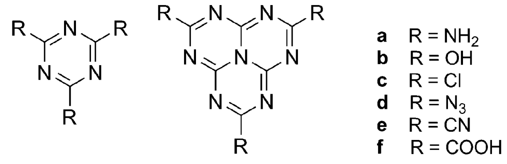
Keywords: *s*-Triazine; Potassium; Carboxylate ligands; Structure elucidation; Metal-organic frameworks

Abstract. Potassium-1,3,5-triazine-2,4,6-tricarboxylate dihydrate $K_3[C_3N_3(COO)_3]\cdot 2H_2O$ was obtained by saponification of the respective ethyl ester in aqueous solution under mild conditions and subsequent crystallization at 4 °C. The crystal structure of the molecular salt was elucidated by single-crystal X-ray diffraction [$P\bar{1}$, a = 696.63(14), b = 1748.5(3), c = 1756.0(3) pm, α = 119.73(3), β = 91.96(3), γ = 93.84(3)°, V = 1847.6(6)·10^6 pm^3, Z = 6, T = 200 K]. Perpendicular to [100] the triazine tricarboxylate and potassium ions are arranged in layers alternating with layers of crystal water molecules. Two thirds of the triazine tricarboxylate units form hexagonal channels being filled with the remaining triazine tricarboxylate molecules. $K_3[C_3N_3(COO)_3]\cdot 2H_2O$ was additionally investigated by means of FTIR spectroscopy, TG and DTA measurements.

Introduction

Research in the field of carbon nitrides is mainly focused on the synthesis of two- and three-dimensional networks, which can serve as functional materials for a wide field of applications such as catalysis or optoelectronic uses [1–3]. A common approach towards multidimensional networks is the pyrolysis of *s*-triazine (C_3N_3) or *s*-heptazine (C_6N_7) based precursors to induce condensation and thereby generating covalently bound products. A variety of precursors with different functional groups has been utilized in this regard (cf. Scheme 1, **1a**–**d** and **2a**–**d**) [4–8].



1 **2**

Scheme 1. Molecular precursors for carbon nitride networks comprising the *s*-triazine (**1**) or *s*-heptazine (**2**) core.

In general, molecules containing residues that are bound to the *s*-triazine or *s*-heptazine core through C–C bonds (cf. Scheme 1, **1e**–**f** and **2e**–**f**) are adverse in this regard. This is due to the strength of the C–C bonds impeding a successful condensation. Furthermore, the synthesis of carbon nitrides necessitates an alternating sequence of carbon and nitrogen both in the precursor and in the resulting polymeric network. Even though such compounds are no suitable precursors for the synthesis of covalently bound true carbon nitrides by condensation reactions they can be regarded as promising linkers in coordination polymers. Metal-organic frameworks (MOFs) have been extensively studied in the last years due to their potential applications, e. g. as materials for ion exchange, separation, catalysis, or gas storage [9, 10]. Whereas numerous MOFs are known in which a hydrocarbon cycle functionalized with several carboxylate groups, e. g. trimesic acid **3** (cf. Scheme 2) [11–13], serves as linker between inorganic atoms or clusters, the analog *s*-triazine or *s*-heptazine compounds **1f** and **2f** have not been employed for this purpose so far.

In known *s*-triazine and *s*-heptazine based linkers such as *s*-triazine-2,4,6-tris(4-pyridyl) (**4**) [14, 15], *s*-triazine-2,4,6-triyl-tribenzoic acid (**5**) [16–20] or *s*-heptazine-2,5,8-triyl-tribenzoic acid (**6**) [20, 21] (cf. Scheme 2), the *s*-triazine or *s*-heptazine cores, respectively, only provide the threefold symmetry but do not contribute to metal coordination. In contrast, in compounds **1f** and **2f** both the carboxylate groups and the nitrogen atoms of the ring can be regarded as coordination positions.

The *s*-heptazine compound **2f** has not been mentioned in the literature so far, whereas the synthesis of **1f** by a multistep reaction via the respective ethyl ester and potassium salt has already been described over 50 years ago [22]. However, no structural characterization of the product or any intermediate was performed and since then only very little research regarding triazine tricarbonic acid or its salts has been carried out until 2002 when *Dunbar* et al. reported the crystal structure and magnetic properties of K{Fe(1,3,5-triazine-2,4,6-tricarboxylate)$(H_2O)_2$}·$2H_2O$ [23].

To the best of our knowledge no crystal structure of any other salt of triazine tricarbonic acid has been described so far.

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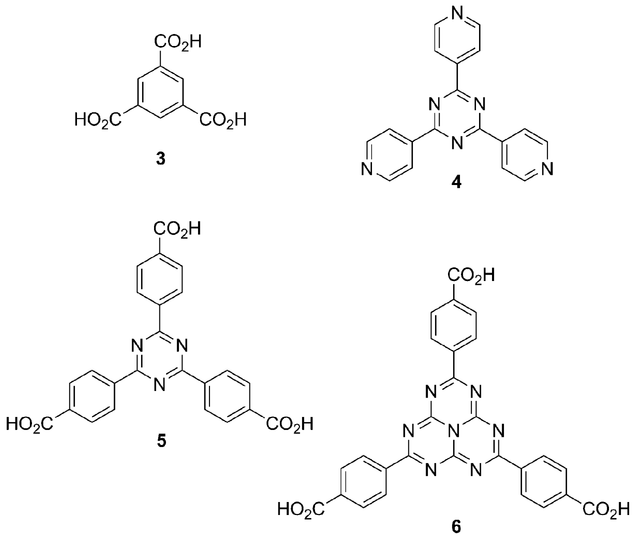

Scheme 2. Multidentate ligands, which are commonly employed as linkers in metal-organic frameworks.

However, regarding the potential application of triazine tricarboxylate as a multidentate ligand, a deeper understanding of its coordination behavior towards various metal ions is of great interest. In this contribution we report on synthesis and crystal structure of potassium triazine tricarboxylate dihydrate $K_3[C_3N_3(COO)_3]\cdot 2H_2O$ as a further example of a structurally characterized triazine tricarboxylate and thereby providing further insight into the coordination properties of this linker.

Table 1. Crystallographic data and details of the structure refinement for $K_3[C_3N_3(COO)_3]\cdot 2H_2O$.

molar mass /g·mol^{-1}	363.41
crystal system	triclinic
space group	$P\bar{1}$ (no. 2)
T /K	200
diffractometer	Nonius Kappa-CCD
radiation, λ /pm	Mo-K_α, 71.073
a /pm	696.63(14)
b /pm	1748.5(3)
c /pm	1756.0(3)
α /°	119.73(3)
β /°	91.96(3)
γ /°	93.84(3)
V /10^6·pm^3	1847.6(8)
Z	6
calculated density /g·cm^{-3}	1.960
crystal size /mm	0.70 × 0.07 × 0.05
absorption coefficient /mm^{-1}	1.150
diffraction range	$3.26° \leq \theta \leq 27.54°$
index range	$-8 \leq h \leq 9$
	$-22 \leq k \leq 22$
	$-22 \leq l \leq 22$
parameters / restraints	577 / 16
total no. of reflections	14291
no. of independent reflections	8452
no. of observed reflections	5617
min./max. residual electron density / 10^6·pm^3	–0.679/ +0.984
GooF	1.047
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0513$, $wR_2 = 0.1068$$^{a)}$
final R indices (all data)	$R_1 = 0.0868$, $wR_2 = 0.1228$$^{a)}$

a) $w = [\sigma^2(F_o^2)+(0.0389P)^2+1.6956P]^{-1}$, with $P = (F_0^2+2F_c^2)/3$.

Results and Discussion

Crystal Structure

Potassium triazine tricarboxylate crystallizes as a dihydrate in the triclinic space group $P\bar{1}$ with six formula units in the unit cell. Crystallographic data and details of the structure refinement are summarized in Table 1. The crystal structure comprises triazine tricarboxylate $[C_3N_3(COO)_3]^{3-}$ and potassium ions and crystal water molecules (cf. Figure 1).

The triazine tricarboxylate ions are nearly planar with only the carboxylate groups being slightly rotated out of plane so that the anions exhibit molecular symmetry C_3. The substituents cause an increase of the adjacent angles (N1–C1–N3 = 124.5°), whereas the remaining angles of the *s*-triazine core are accordingly reduced (C1–N1–C2 = 115.5°). In accordance with expectation, the bond lengths of both the C–N bonds within the ring (133–134 pm) and the C–O bonds of the carboxylate groups (124–125 pm) correspond to conjugated double bonds, whereas the C–C bond lengths of 153–154 pm resemble those of single bonds (cf. Table 2).

The triazine tricarboxylate ions, the potassium atoms, and water molecules are arranged in an AA'BB' type stacking pattern perpendicular to [100] (cf. Figure 2) with the A and A' layers consisting of the triazine tricarboxylate and potassium ions and the crystal water molecules being located in the intermediate B and B' layers. Within the A and A' layers the triazine tricarboxylate ions are not coplanar but are slightly tilted out of the *bc* plane. Perpendicular to [100] the triazine tricarboxylate units form two different kinds of columns. One third of the columns consist solely of molecules B (cf. Figure 1) with the molecules of two adjacent layers A and A' being rotated by 60° within the plane. In the remaining columns molecules A and C alternate and are rotated by 30°. These columns form hexagonal channels around the B columns (cf. Figure 3).

The interlayer distance of 347 pm between two triazine tricarboxylate layers is in the expected range for molecular *s*-triazine derivatives [1, 24, 25]. Between the layers the triazine tricarboxylate units are interconnected by a network of medium strong [26] hydrogen bonds (cf. Table 3) by the carboxylate groups. All crystal water molecules are part of the hydrogen bonding network although due to the strong disorder of one oxygen atom (O24) no hydrogen bond can be clearly assigned to the linked hydrogen atom H11.

The potassium ions are coordinated in the form of irregular polyhedrons by four to six oxygen atoms of water molecules and carboxylate groups and by one nitrogen atom of the triazine rings. The triazine tricarboxylate units serve as tridentate ligands and coordinate the K^+ atoms through the O–N–O entities (cf. Figure 1) with the K^+ atom being slightly shifted towards one of the oxygen atoms. The coordination sphere is completed by the oxygen atoms of further triazine tricarboxylate units and water molecules. The K–O distances (273–297 pm) are in accordance with the sum of the ionic radii [27]

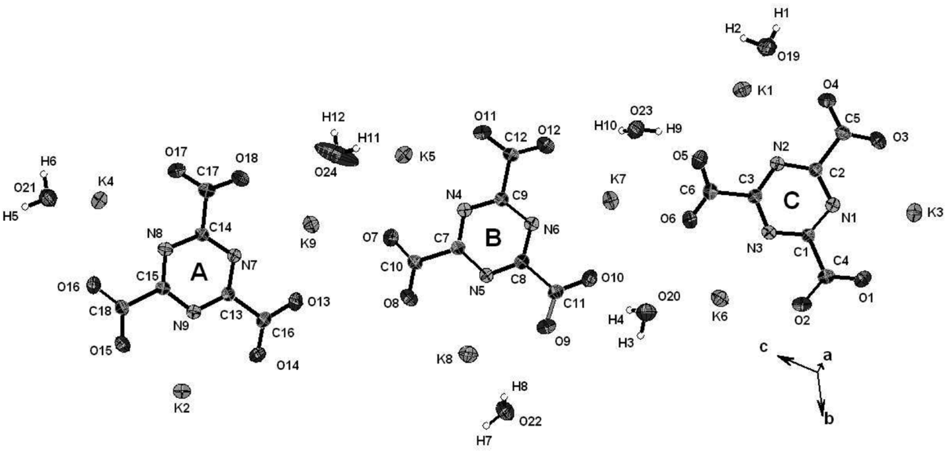

Figure 1. Representation of one formula unit of $K_3[C_3N_3(COO)_3]{\cdot}2H_2O$. The three triazine tricarboxylate entities present in the crystal structure are labeled A–C. Thermal ellipsoids (except for hydrogen) are drawn at the 50 % probability level.

Table 2. Selected bond lengths /pm and angles /° in $K_3[C_3N_3(COO)_3]{\cdot}2H_2O$, standard deviations in parentheses.

K1– O4	292.6(3)	K3– O16	281.0(3)	K5– N4	278.2(3)	K8– O8	284.0(3)	N3– C3	132.9(4)	N2– C2– C5	117.9(3)
K1– O5	281.7(3)	K3– O16	283.7(3)	K6– O2	278.6(3)	K8– O9	296.2(3)	C4– O1	123.9(4)	N2– C3– C6	118.2(3)
K1– O14	279.1(3)	K3– O21	282.2(3)	K6– O6	287.2(3)	K8– O22	278.2(3)	C4– O2	125.0(4)	N3– C3– C6	117.3(3)
K1– O14	284.6(3)	K3– N1	279.7(3)	K6– O18	280.0(3)	K8– N5	279.7(3)	C1– C4	153.0(4)	O1– C4– O2	127.5(3)
K1– O19	280.3(3)	K4– O1	287.5(3)	K6– O18	293.0(3)	K9– O7	274.4(3)	C2– C5	154.2(5)	O4– C5– O3	127.8(3)
K1– N2	278.6(3)	K4– O9	276.9(3)	K6– O20	285.4(4)	K9– O13	274.0(3)	C3– C6	153.0(5)	O6– C6– O5	128.5(4)
K2– O4	286.3(3)	K4– O16	290.3(3)	K6– O24	284.7(4)	K9– O18	297.1(3)	C2– N1– C1	115.4(3)	O1– C4– C1	117.5(3)
K2– O12	281.2(3)	K4– O17	286.5(3)	K6– N3	279.3(3)	K9– O20	275.7(3)	C2– N2– C3	115.4(3)	O2– C4– C1	115.0(3)
K2– O14	284.4(3)	K4– O21	273.4(3)	K7– O6	277.8(3)	K9– O24	274.0(4)	C3– N3– C1	115.7(3)	O3– C5– C2	115.2(3)
K2– O15	283.0(3)	K4– O22	279.3(3)	K7– O10	276.2(3)	K9– N7	281.8(3)	N3– C1– N1	124.3(3)	O4– C5– C2	117.0(3)
K2– O19	275.7(3)	K4– N8	281.8(3)	K7– O12	291.8(3)	N1– C1	133.8(4)	N2– C2– N1	124.7(3)	O5– C6– C3	115.3(3)
K2– O23	273.4(3)	K5– O1	280.5(3)	K7– O19	295.5(3)	N1– C2	133.4(4)	N3– C3– N2	124.5(3)	O6– C6– C3	116.1(3)
K2– N9	280.7(3)	K5– O7	291.3(3)	K7– O23	285.2(3)	N2– C2	133.1(4)	N1– C1– C4	117.9(3)		
K3– O1	287.6(3)	K5– O11	277.1(3)	K7– N6	279.1(3)	N2– C3	133.9(4)	N3– C1– C4	117.8(3)		
K3– O3	281.1(3)	K5– O24	280.0(5)	K8– O4	278.7(3)	N3– C1	133.6(4)	N1– C2– C5	117.4(3)		

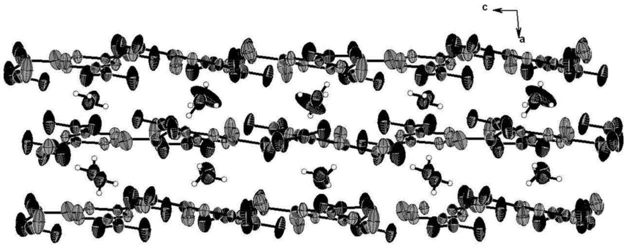

Figure 2. Crystal structure of $K_3[C_3N_3(COO)_3]{\cdot}2H_2O$ representing the layered structure perpendicular to [100]. Thermal ellipsoids (except for hydrogen) are drawn at the 50 % probability level.

whereas the K–N distances (278–282 pm) are relatively short compared to the potassium salts of other *s*-triazine or *s*-heptazine compounds [28–30]. In K{Fe(1,3,5-triazine-2,4,6-tricarboxylate)$(H_2O)_2$}·$2H_2O$, the iron atoms are coordinated by an O–N–O unit in a similar way as in the title compound with a short Fe–N distance of 212 pm, whereas the potassium ions are coordinated solely by oxygen atoms and the K–O distances are comparable in both compounds. Hence, in both triazine tricarboxylate salts a strong contribution of the *s*-triazine core to metal coordination is observed so that the triazine tricarboxylate unit can be regarded as an interesting linker for coordination networks potentially allowing other linkage motifs than those observed in MOFs, which contain trimesic acid as the organic linker.

Vibrational Spectroscopy

Potassium triazine tricarboxylate dihydrate was analyzed by FTIR spectroscopy. All signals in the spectrum can be attributed to vibrations of the triazine tricarboxylate entities and water molecules, respectively (cf. Figure 4). The bending and stretching vibrations of the *s*-triazine ring lead to a characteristic absorption band at 740 cm^{-1} and a group of signals at 1300–1660 cm^{-1}, respectively. In the range between 1300 and 1660 cm^{-1}, the stretching vibrations of the carboxylate groups can be observed as well. The broad band at 3000–3600 cm^{-1} can be attributed to the OH stretching vibrations of the crystal water molecules and in accordance with the crystal structure the redshift of the ν(OH) signals corresponds to medium strong hydrogen bonds [26].

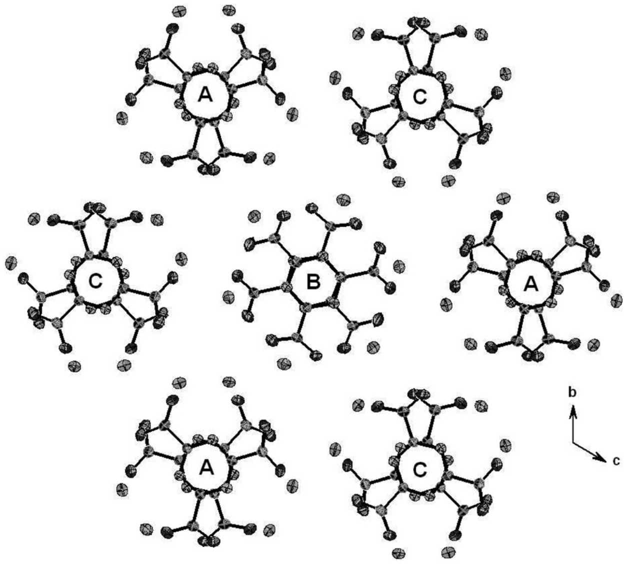

Figure 3. Crystal structure of $K_3[C_3N_3(COO)_3]\cdot 2H_2O$ representing the stacked arrangement of the triazine tricarboxylate entities. Crystal water molecules are omitted for clarity. The labels A–C refer to Figure 1, indicating, which triazine tricarboxylate unit lies on top of the respective column. Thermal ellipsoids are drawn at the 50 % probability level.

Table 3. Donor-acceptor distances /pm and donor-hydrogen-acceptor angles /° for the hydrogen bonding network in $K_3[C_3N_3(COO)_3]\cdot 2H_2O$.

D–H···A	D···A	<D–H···A	D–H···A	D···A	<D–H···A
O19–H1···O8	283.9	154.79	O22–H7···O15	266.5	173.09
O19–H2···O5	272.0	159.35	O22–H8···O11	292.8	176.50
O20–H3···O2	277.5	152.52	O23–H9···O13	269.0	157.25
O20–H4···O10	279.6	166.63	O23–H10···O8	290.1	167.27
O21–H5···O3	270.6	160.13	O24–H12···O17	266.6	155.49
O21–H6···O11	281.4	169.61			

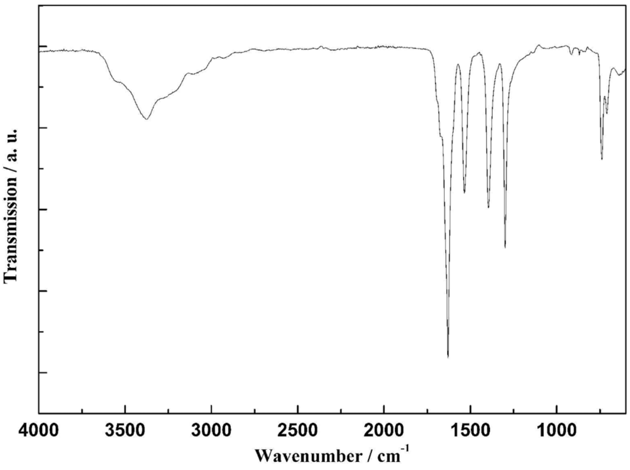

Figure 4. FTIR spectrum of $K_3[C_3N_3(COO)_3]\cdot 2H_2O$.

Thermal Behavior

TG and DTA curves of potassium triazine tricarboxylate dihydrate are displayed in Figure 5. In the temperature range between 65 and 150 °C, the crystal water molecules are released (mass loss observed: 10.9 %, calculated: 9.9 %) and the so obtained dehydrated compound is thermally stable up to 325 °C. The decomposition of the sample starts with a mass loss of 17 % accompanied by a sharp endothermic signal at 325–390 °C, probably due to a partial decarboxylation, and proceeds with a slow and steady mass loss at higher temperatures.

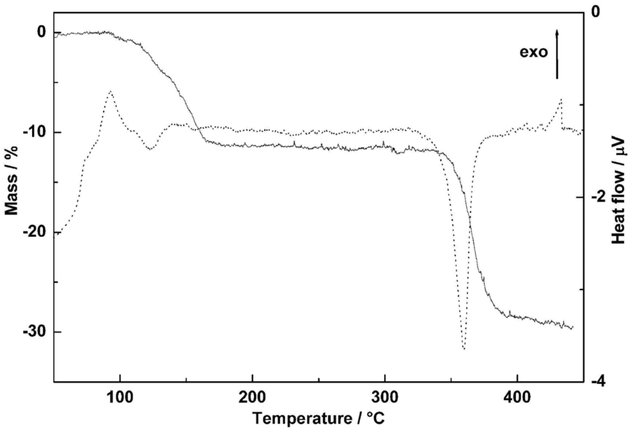

Figure 5. TG (solid) and DTA (dotted) curves of $K_3[C_3N_3(COO)_3]\cdot 2H_2O$, recorded with a heating rate of 5 °C min^{-1}.

Conclusions

We reported on the crystal structure and thermal behavior of potassium triazine tricarboxylate dihydrate. Triazine tricarboxylate represents a multidentate ligand, which can be regarded as the *s*-triazine analog of trimesic acid and hence as a promising linker for metal-organic frameworks but only one triazine tricarboxylate salt has been structurally characterized so far. This study has expanded the investigations of this class of compounds to a new salt and thereby provides further insight into the coordination properties of triazine tricarboxylate. The presented crystal structure shows that the nitrogen atoms of the *s*-triazine cycle exhibit a strong interaction with the potassium ions and that the coordination of metal ions through the O–N–O units of the triazine tricarboxylate entities is a recurring binding motif for this ligand. Because of the differing coordination properties compared to trimesic acid, triazine tricarboxylate seems to be an interesting linker for coordination networks and with the observed high thermal stability of $K_3[C_3N_3(COO)_3]$ an important condition for syntheses of three-dimensional networks at elevated temperatures is fulfilled.

Experimental Section

Syntheses

Potassium triazine tricarboxylate dihydrate was synthesized according to the procedure described in [22, 31] by saponification of the respective triethyl ester. To prepare the triethyl ester, dry HCl was conducted through ethyl cyanoformate (20.0 g, 202 mmol, Aldrich, 99 %) under argon until the trimerization product started to precipitate. Afterwards, the conversion was completed by cooling the reaction mixture to 4 °C overnight. The product was filtered, washed with cold water and dried at 75 °C to yield 7.15 g (24.1 mmol, 36 %) triethyl-*s*-triazine-2,4,6-tricarboxylate as colorless needles. Elemental analysis: N 14.22 (calcd. 14.13), C 47.20 (calcd. 48.47), H 4.88 (calcd. 5.08) %.

Small amounts of the triethyl ester (100 mg, 0.34 mmol) were added to KOH (3.5 mL of a 1 M aqueous solution), while cooling with an ice bath. The reaction was stirred until the ester was completely dissolved. Afterwards, ethanol (25 mL) was poured into the solution to precipitate the potassium salt. The product was filtered, washed with ethanol and dried at 75 °C to obtain potassium-1,3,5-triazine-2,4,6-tricarboxylate dihydrate (103 mg, 0.28 mmol) as colorless needles. Yield 83 %. Single crystals suitable for single-crystal X-ray diffraction were obtained by repeated recrystallization from aqueous solution at 4 °C. Elemental analysis: N 11.60 (calcd. 11.56), C 20.45 (calcd. 19.83), H 0.64 (calcd. 1.11) %.

X-ray Structure Determination

Single-crystal X-ray diffraction data of $K_3[C_3N_3(COO)_3]\cdot 2H_2O$ were collected at 200 K with a Kappa CCD diffractometer using monochromated Mo-K_α radiation (λ = 71.073 pm). The diffraction intensities were scaled using the SCALEPACK software package [32] and no additional adsorption correction was applied. The crystal structure was solved by direct methods using the software package SHELXS-97 [33] and refined against F^2 by applying the full-matrix least-squares method (SHELXL-97) [34]. The hydrogen positions could be determined from difference Fourier syntheses and were refined isotropically using restraints for oxygen–hydrogen distances. All non-hydrogen atoms were refined anisotropically.

CCDC-784049 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; or E-Mail: deposit@ccdc.cam.ac.uk).

FT-Infrared Spectroscopy

A FTIR spectrum was recorded at ambient conditions between 600 and 4500 cm^{-1} with a Spektrum BX II FTIR spectrometer (Perkin–Elmer) equipped with a DuraSampler diamond ATR device.

Thermal Analysis

Thermoanalytical measurements were performed with a Thermoanalyzer TG-DTA92 (Setaram) under inert atmosphere (helium). The sample was heated in an alumina crucible from room temperature to 500 °C with a heating rate of 5 $°C\cdot min^{-1}$.

Acknowledgement

The authors thank the *Deutsche Forschungsgemeinschaft* (DFG) (project SCHN 377/12) and the *Fonds der Chemischen Industrie* (FCI) for financial support and *Dr. Peter Mayer* (Department Chemie, LMU München) for the single-crystal data collection.

References

[1] G. Goglio, D. Foy, G. Demazeau, *Mater Sci. Eng.* **2008**, *58*, 195.
[2] E. Kroke, M. Schwarz, *Coord. Chem. Rev.* **2004**, *248*, 493.
[3] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl, J. M. Carlsson, *J. Mater. Chem.* **2008**, *18*, 4893.
[4] E. G. Gillan, *Chem. Mater.* **2000**, *12*, 3906.
[5] T. Komatsu, *J. Mater. Chem.* **2001**, *11*, 799.
[6] E. Kroke, M. Schwarz, E. Horath-Bordon, P. Kroll, B. Noll, A. D. Norman, *New J. Chem.* **2002**, *26*, 508.
[7] B. V. Lotsch, M. Döblinger, J. Sehnert, L. Seyfarth, J. Senker, O. Oeckler, W. Schnick, *Chem. Eur. J.* **2007**, *13*, 4969.
[8] D. R. Miller, J. R. Holst, E. G. Gillan, *Inorg. Chem.* **2007**, *46*, 2767.
[9] A. U. Czaja, N. Trukhan, U. Müller, *Chem. Soc. Rev.* **2009**, *38*, 1284.
[10] R. J. Kuppler, D. J. Timmons, Q.-R. Fang, J.-R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, H.-C. Zhou, *Coord. Chem. Rev.* **2009**, *253*, 3042.
[11] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148.
[12] 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.
[13] O. M. Yaghi, G. Li, H. Li, *Nature* **1995**, *378*, 703.
[14] D. N. Dybtsev, H. Chun, K. Kim, *Chem. Commun.* **2004**, 1594.
[15] M.-X. Li, Z.-X. Miao, M. Shao, S.-W. Liang, S.-R. Zhu, *Inorg. Chem.* **2008**, *47*, 4481.
[16] D. Sun, S. Ma, Y. Ke, T. M. Petersen, H.-C. Zhou, *Chem. Commun.* **2005**, 2663.
[17] Y. K. Park, S. B. Choi, H. Kim, K. Kim, B.-H. Won, K. Choi, J.-S. Choi, W.-S. Ahn, N. Won, S. Kim, D. H. Jung, S.-H. Choi, G.-H. Kim, S.-S. Cha, Y. H. Jhon, J. K. Yang, J. Kim, *Angew. Chem.* **2007**, *119*, 8378; *Angew. Chem. Int. Ed.* **2007**, *46*, 8230.
[18] S. Ma, X.-S. Wang, D. Yuan, H.-C. Zhou, *Angew. Chem.* **2008**, *120*, 4198; *Angew. Chem. Int. Ed.* **2008**, *47*, 4130.
[19] D. Sun, S. Ma, Y. Ke, D. J. Collins, H.-C. Zhou, *J. Am. Chem. Soc.* **2006**, *1258*, 3896.
[20] S. Ma, D. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin, H.-C. Zhou, *J. Am. Chem. Soc.* **2007**, *129*, 1858.
[21] Y. Ke, D. J. Collins, D. Sun, H.-C. Zhou, *Inorg. Chem.* **2006**, *45*, 1897.
[22] C. Grundmann, E. Kober, *J. Org. Chem.* **1956**, *21*, 1392.
[23] J.-R. Galán-Mascarós, J.-M. Clemente-Juan, K. R. Dunbar, *J. Chem. Soc., Dalton Trans.* **2002**, *13*, 2710.
[24] S.-J. Chen, U. Behrens, E. Fischer, R. Mews, F. Pauer, G. M. Sheldrick, D. Stalke, W.-D. Stohrer, *Chem. Ber.* **1993**, *126*, 2601.
[25] B. V. Lotsch, W. Schnick, *Chem. Mater.* **2006**, *18*, 1891.
[26] T. Steiner, *Angew. Chem.* **2002**, *114*, 50; *Angew. Chem. Int. Ed.* **2002**, *41*, 48.
[27] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.
[28] E. Horvath-Bordon, E. Kroke, I. Svoboda, H. Fueß, R. Riedel, S. Neeraj, A. K. Cheetham, *Dalton Trans.* **2004**, 3900.
[29] E. Irran, B. Jürgens, W. Schnick, *Chem. Eur. J.* **2001**, *7*, 5372.
[30] A. Sattler, W. Schnick, *Eur. J. Inorg. Chem.* **2009**, 4972.
[31] E. Ott, *Ber. Dtsch. Chem. Ges.* **1919**, *52*, 656.
[32] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.
[33] G. M. Sheldrick, *SHELXS-97*, Program for the Solution of Crystal Structures, Universität Göttingen, Germany **1997**.
[34] G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures, Universität Göttingen, Germany **1997**.

Received: June 18, 2010