Non-centrosymmetric Coordination Polymers Based on Thallium and Acetylenedicarboxylate

Running Head: Thallium Acetylenedicarboxylates

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Dedicated to Prof. Dr. L. Bohatý on the occasion of his 60th birthday.

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Abstract

Single crystals of anhydrous thallium acetylenedicarboxylate ($\text{Tl}_2(\text{C}_4\text{O}_4)$, **1**) and thallium acetylenedicarboxylate oxalate ($\text{Tl}_4(\text{C}_4\text{O}_4)(\text{C}_2\text{O}_4)$, **2**) precipitated from aqueous solutions containing thallium(I)-acetate and the respective organic acids. Both compounds crystallize in non-centrosymmetric space groups (**1**: $P 2_1 2_1 2_1$; **2**: $C 2$), which is probably caused by stereochemically active lone pairs at Tl(I). The crystal structures of **1** and **2** show some similarities. Tl atoms are organized in corrugated layers, which are connected by the respective carboxylate anions. Upon heating **1** decomposes at 195°C to form elemental pyrophorous thallium powder. **2** starts decomposing at approx. 150°C forming elemental thallium next to another compound, which could not be identified up to now. TIHADC was also synthesized, but its crystal structure could not be solved either from powder or single crystal diffraction data. Upon heating it decomposes to form **1**.

Keywords

Acetylenedicarboxylate, Coordination polymer, Noncentrosymmetric crystal structures, Thallium, Thermal analysis

1. Introduction

Coordination polymers based on polycarboxylic acids are one of the most important topics of modern solid state chemistry. Especially porous compounds like MOF-5 [1], MIL-53 [2] or HKUST-1 [3] have attracted a lot of attention due to their potential as heterogenous catalysts or adsorbates for gases like hydrogen. But besides porosity there are also attractive aspects of non-porous coordination polymers in the field of magnetic, luminescent or conducting properties to name a few [4]. From a more fundamental point of view coordination polymers are also in the focus of modern solid state chemistry, as the rational design of new solid state compounds, i.e. the construction of pre-designed products starting from simple components, seems to be within reach for this class of compounds. Metal ions with a given coordination geometry – i.e. tetrahedral or octahedral – connected via a linear bifunctional ligand should lead to topologies known from simple salts or compounds, like e.g. diamond or α -Po [5]. By modifying the connecting ligand a further tailoring of the structure is possible, as was shown by *O. Yaghi et al.* [6].

An interesting aspect in this context is the rational design of non-centrosymmetric coordination polymers. Several concepts have been successfully used based on diamondoid networks [7] or kinked ligands [8]. Beside these successful strategies there are also concepts to increase the probability to crystallize a compound in a non-centrosymmetric space group. We showed that coordination polymers containing a linear and a trigonal planar anion show an enhanced probability to crystallize in non-centrosymmetric space groups [9]. This simple concept was confirmed by the results of other groups [10]. In another approach it was shown that compounds containing a cation with a stereochemically active lone pair also show an enhanced probability to crystallize in non-centrosymmetric space group [11].

In the following we will present two new coordination polymers based on Tl^+ and the dianion of acetylenedicarboxylic acid ($HOOC-C\equiv C-COOH = H_2ADC$). In both compounds the lone

pair of Tl^+ is stereochemically active and these compounds crystallize in non-centrosymmetric space groups.

2. Synthesis

Caution!!! Thallium compounds are highly toxic. Therefore adequate safety precautions have to be used before handling thallium compounds.

Tl_2ADC ($\text{ADC}^{2-} \equiv \text{acetylenedicarboxylate}, ^-\text{OOC}-\text{C}\equiv\text{C}-\text{COO}^-$): 0.527 g (2 mmol) thallium(I)-acetate (Merck) and 0.114 g (1 mmol) acetylenedicarboxylic acid (Fluka, $\geq 98\%$) were dissolved in 8 ml deionized water. The beaker was sealed with a perforated foil. After two days at 295 K a colorless precipitate had formed, from which single crystals of Tl_2ADC were isolated. The precipitate is single-phase, as was confirmed by X-ray powder diffraction (Huber G 670, $\text{CuK}\alpha_1$ radiation) and chemical analysis (calc. for $\text{C}_4\text{O}_4\text{Tl}_2$ (520.78): C 9.22 %; found: C 9.41 %). No yield was determined.

TlHADC : 0.527 g (2 mmol) thallium(I)-acetate (Merck) and 0.228 g (2 mmol) acetylenedicarboxylic acid (Fluka, $\geq 98\%$) were dissolved in 8 ml deionized water. The beaker was sealed with a perforated foil. After one day at 274 K a colorless precipitate had formed, from which several crystals of TlHADC were isolated. But all of them were twinned so that no reasonable structural model could be determined. From X-ray powder diffraction patterns (Huber G 670, $\text{CuK}\alpha_1$ radiation) of the precipitate a unit cell similar to those found in the X-ray single-crystal structure analysis was obtained ($a \approx 10.89 \text{ \AA}$, $c \approx 8.02 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$). But a complete structural model could not be developed. It was only possible to localize the Tl atoms. The localization of the HADC^- anions next to the heavy scatterer Tl was not successful up to now. According to the chemical analysis (calc. for $\text{C}_4\text{HO}_4\text{Tl}$ (317.42): C

15.13 %, H 0.32 %; found: C 15.25 %, H 0.18 %) the sample is single-phase. No yield was determined.

Tl₄(ADC)(oxa) (oxa²⁻ $\equiv$ oxalate, ⁻OOC-COO⁻): 0.527 g (2 mmol) thallium(I)-acetate (Merck), 0.045 g (0.5 mmol) oxalic acid (Merck) and 0.057 g (0.5 mmol) acetylenedicarboxylic acid (Fluka, $\geq$ 98 %) were dissolved in 15 ml deionized water. The beaker was sealed with a perforated foil. After ten days at 295 K a colorless precipitate had formed, from which single crystals of Tl₄(ADC)(oxa) were isolated. The precipitate is single-phase, as was confirmed by X-ray powder diffraction (Huber G 670, CuK α ₁ radiation) and chemical analysis (calc. for C₆O₈Tl₄ (1017.54): C 7.08 %; found: C 7.26 %). No yield was determined.

A first single crystal of Tl₄(ADC)(oxa) was obtained from a solution containing 0.02 g (0.5 mmol) LiOH · H₂O, 0.13 g (0.5 mmol) thallium(I)-acetate, and 0.06 g (0.5 mmol) acetylenedicarboxylic acid in 2 ml of deionized water in a beaker sealed with a perforated foil. After three days at slightly elevated temperatures (approx. 305 K) a precipitate formed, from which a single crystal of Tl₄(ADC)(oxa) was isolated. After its structural solution the improved synthesis given above was developed.

3. Crystal Structure

Single crystals of Tl₂ADC and Tl₄(ADC)(oxa) were isolated and sealed in glass capillaries. Reflection intensities were collected on a Stoe IPDS II diffractometer (graphite monochromatized MoK α radiation) at room temperature. For data collection and reduction the Stoe program package [12] was applied. The structural models were solved using SIR-92 [13] and completed using difference fourier maps calculated with SHELXL-97 [14], which was also used for the final refinement. All programs were run under the WinGX system [15].

More details of the structural analysis [16] are given in Table 1. All atoms were refined anisotropically. In Table 2 selected interatomic distances and angles are listed.

< Table 1 >

< Table 2 >

Tl₂ADC. The coordination spheres around Tl1 and Tl2 are shown in Figure 1. Taking Tl-O distances below 3.1 Å into account Tl1 is 6-coordinate (Tl – O: 2.756 – 2.99 Å) and Tl2 is 5-coordinate (Tl – O: 2.635 – 3.014 Å). Using the bond valence sum formalism [17] the following valences are calculated: $V(\text{Tl1}) = 0.94$ and $V(\text{Tl2}) = 0.93$. This is close to the expected value for monovalent Tl. Adding the next-nearest neighbours as given in Table 2 these values increase slightly, but the influence of these next-nearest neighbours remains small, so that these oxygen atoms are not considered being part of the first coordination sphere of Tl1 and Tl2.

Figure 1: ORTEP diagrams of the coordination spheres around Tl1 (left) and Tl2 (right) in Tl₂ADC showing 50% probability thermal ellipsoids and the atom-numbering scheme. Tl-O bonds are drawn as broken lines.

From Figure 1 it is obvious that the coordination spheres of Tl1 and especially Tl2 are very unsymmetric. One part of the sphere remains uncoordinated, which is typical for a

stereochemically active lone pair. This can also nicely be seen in Figure 2, where the uncoordinated part of the coordination sphere is very obvious. We think that these stereochemically active lone pairs are the reason that Tl_2ADC crystallizes in a non-centrosymmetric space group. A similar behaviour was found for other compounds with lone pairs [11]. But it must be pointed out that stereochemically active lone pairs only increase the probability of getting a compound crystallizing in a non-centrosymmetric space group, they do not lead necessarily to acentric crystals.

To investigate the NLO properties of Tl_2ADC in more detail we grew larger single crystals with sizes up to several millimeters. But when attempting to measure the SHG effect we found that these crystals decompose in the laser beam releasing a fine dust. Due to the toxicity of Tl compounds we did not follow up these experiments any longer.

In Figure 2 a larger part of the crystal structure of Tl_2ADC is shown. The ADC^{2-} anions are aligned more or less parallel to each other along the [001] axis. This behaviour is typical for coordination polymers of acetylenedicarboxylates with low valent cations. Only with higher valent cations (e.g. trivalent rare earth metals [18]) it was found that the ADC^{2-} anions are aligned perpendicular to each other.

Figure 2: Packing diagram of Tl_2ADC in a projection along $[100]$ (Tl: large blue spheres, O: small red spheres, C: small white spheres). Tl-O bonds are drawn as broken lines.

In the crystal structure of Tl_2ADC the Tl atoms are organized in corrugated layers along (001). Within these layers the Tl atoms are connected by oxygen atoms of the ADC^{2-} anions. These layers are connected by the carbon backbones of the anions so that a three-dimensional framework structure is formed. The distances and angles within the ADC^{2-} anion show the expected values as given in Table 2. Due to the strong scattering power of Tl the accuracy of these bonds and angles is low, i.e. the standard deviations are high. Thus, they will not be discussed any further.

TIHADC. Tl_2ADC was obtained from a solution containing Tl^+ and H_2ADC in a 2:1 ratio. Using a 1:1 ratio a precipitate was obtained, which – according to the chemical analysis – consists of TIHADC. But unfortunately, no single crystal suitable for a single crystal structure analysis could be isolated. All crystals investigated up to now were twinned. A trigonal or

hexagonal unit cell with $a \approx 10.9 \text{ \AA}$ and $c \approx 8.0 \text{ \AA}$ was found, but no reasonable structural model could be determined. From the unit cell volume $Z = 6$ can be estimated. A similar unit cell was obtained from X-ray powder diffraction data. But again a structural solution failed. Only Tl positions could be localized (e.g. Tl1 0 0 0.272, Tl2 $1/3 \ 2/3 \ 0.333$, Tl3 $2/3 \ 1/3 \ 0.384$ in $P 6_3$). However, the determination of the anion positions did not lead to a reasonable structural model. Therefore, at this point, no further information can be given on the crystal structure of TIHADC.

Tl₄(ADC)(oxa). The coordination spheres around Tl1 and Tl2 are shown in Figure 3. Taking Tl-O distances below $3.1 \text{ \AA}$ into account Tl1 and Tl2 are 5-coordinate (Tl1 – O: $2.673 - 2.918 \text{ \AA}$; Tl2 – O: $2.572 - 3.005 \text{ \AA}$). Using the bond valence sum formalism [17] the following valences are calculated: $V(\text{Tl1}) = 1.01$ and $V(\text{Tl2}) = 0.97$. This is again close to the expected value for monovalent Tl. Adding the next-nearest neighbours as given in Table 2 these values increase slightly, but the influence of these next-nearest neighbours remains small, so that these oxygen atoms are not considered being part of the first coordination sphere of Tl1 and Tl2.

Figure 3: ORTEP diagrams of the coordination spheres around Tl1 (left) and Tl2 (right) in $\text{Tl}_4(\text{ADC})(\text{oxa})$ showing 50% probability thermal ellipsoids and the atom-numbering scheme. Tl-O bonds are drawn as broken lines.

From Figure 3 it is obvious that the coordination spheres of Tl1 and Tl2 are also very unsymmetric. Uncoordinated parts in the coordination spheres point to stereochemically active lone pairs. This can also nicely be seen in Figure 4. As for Tl_2ADC these stereochemically active lone pairs lead to the crystallization in a non-centrosymmetric space group. As Tl_2ADC decomposed in the laser beam, we did not attempt to investigate the SHG effect of $\text{Tl}_4(\text{ADC})(\text{oxa})$.

In Figure 4 a larger part of the crystal structure of $\text{Tl}_4(\text{ADC})(\text{oxa})$ is shown. Again the ADC^{2-} anions are aligned parallel to each other. The Tl atoms form corrugated layers along (100). Within these layers the Tl atoms are connected by oxygen atoms of the carboxylate anions. These layers are connected by the carbon backbones of the anions so that a three-dimensional framework structure is formed. The crystal structures of Tl_2ADC and $\text{Tl}_4(\text{ADC})(\text{oxa})$ show some similarities, which will be discussed later on. But it is intriguing that $\text{Tl}_4(\text{ADC})(\text{oxa})$ can be synthesized without adding oxalic acid. That means H_2ADC has been oxidized under very mild reaction conditions to form oxalic acid. It would be interesting to understand this reaction mechanism in more detail.

The distances and angles within the ADC^{2-} and oxalate anions show the expected values as given in Table 2. Due to the strong scattering power of Tl the standard deviations of these bonds and angles are high, so that they will not be discussed any further.

Figure 4: Packing diagram of $\text{Tl}_4(\text{ADC})(\text{oxa})$ in a projection along $[010]$ (Tl: large blue spheres, O: small red spheres, C: small white spheres). Tl-O bonds are drawn as broken lines.

4. Thermoanalytical Investigations

DTA/TG investigations were performed on Tl_2ADC and TlHADC using a Netzsch STA 409C housed in a glovebox (Fa. Braun, Garching/Germany).

For Tl_2ADC a very sharp exothermic signal was observed at 194°C , which was accompanied by a weight loss of approx. 8.3 %. This corresponds to the loss of one CO_2 molecule per formula unit (calc.: 8.45 %).

For TIHADC a very strong exothermic decomposition was observed at 128°C. During this explosion-like process some sample was expelled from the sample holder so that no reliable TG data were obtained.

To understand the thermal behaviour of these compounds in more detail temperature-dependent synchrotron powder diffraction data were recorded, which are given in the next chapter.

5. Temperature Dependent Synchrotron Powder Diffraction

For SrADC we found a small negative thermal expansion below room temperature [19] and above [20]. A so-called “guitar string vibration” [21] of bridging oxygen atoms was identified as a possible fingerprint for this unusual behavior in SrADC. Therefore we were interested to check whether a similar behaviour occurs in anhydrous Ti_2ADC .

High-temperature synchrotron powder investigations were performed at the powder diffractometer of beamline B2 of the Hamburg synchrotron facility (HASYLAB) using the following set-up: $\lambda = 0.47211 \text{ \AA}$ (Ti_2ADC , TIHADC) and $\lambda = 0.68541 \text{ \AA}$ ($\text{Ti}_4(\text{ADC})(\text{oxa})$); position sensitive imaging plate detector system (OBI [22]); STOE capillary furnace. The exposure time of each diffraction pattern was corrected for fluctuations and decay of the synchrotron beam by using monitor counts collected between the incident beam and the sample. The samples were filled in glass capillaries ($\varnothing = 0.3 \text{ mm}$), the funnel was closed with picein. The actual temperature of the furnace was obtained from the temperature dependence of the lattice parameter of NaCl, which was measured as a standard prior to the measurements. All diffractograms were analysed using the STOE software Win XPOW [23]. For the Rietveld refinements the GSAS software package was applied [24]. To obtain reliable trends of the

lattice parameters the same sets of variables were used in the final Rietveld refinements of all diffractograms.

Diffractograms of Tl_2ADC were recorded between 30°C and 240°C using 30°C steps. Tl_2ADC is stable up to 180°C, all lattice parameters increase with increasing temperature. At approx. 195°C Tl_2ADC decomposes in a violent reaction forming a black residue. This residue inflames on air. According to the synchrotron pattern obtained after cooling (Figure 5) the residue contains elemental thallium in its high ($\text{Im}\bar{3}\text{m}$, $Z = 2$; 86 wt.%) and room temperature modifications ($\text{P6}_3/\text{mmc}$, $Z = 2$; 14 wt.%). As probably a very fine thallium powder (“thallium sponge”) is obtained, the residue is pyrophorous. We assume that CO_2 is released in this decomposition reaction, whereas the remaining carbon forms an amorphous solid:

The decomposition temperature is in good agreement with the results of the DTA/TG investigations, but here the release of only one molecule CO_2 per formula unit was calculated. Thus, the correct reaction mechanism remains unclear at this point, but we were able to reproduce the results above by heating larger amounts of Tl_2ADC in an argon atmosphere up to 240°C. Again a black powder was obtained, which contains elemental thallium according to XRPD investigations.

Figure 5: Synchrotron powder diffraction pattern (HASYLAB, beamline B2, $\lambda = 0.47211 \text{ \AA}$, OBI detector system, capillary $\varnothing 0.3 \text{ mm}$) of the residue of Tl_2ADC after heating at 240°C showing the observed (+) and calculated patterns (solid line) as well as the difference between them. Vertical bars mark the positions of the reflections of HT-Thallium (lower bars) and RT-Thallium (upper bars).

TIHADC was investigated between 30°C and 300°C in 30°C steps (Figure 6). Up to 90°C most reflections could be indexed in a hexagonal unit cell with $a \approx 10.9 \text{ \AA}$ and $c \approx 8.0 \text{ \AA}$ (s. above). Lattice parameter a increases with increasing temperature, whereas c slightly decreases. But the unit cell volume shows a usual positive thermal expansion. At 120°C TIHADC transforms completely to Tl_2ADC . No additional reflections are found in the diffraction patterns. Thus, the following reaction scheme is likely:

As no reflections of H_2ADC ($\text{H}_2\text{C}_4\text{O}_4$) can be observed, it probably decomposes to yield C_2H_2 and two CO_2 molecules. A similar reaction was found for $(\text{NH}_4)_2(\text{C}_4\text{O}_4)$ [25]. Between 190 and 210°C Tl_2ADC decomposes in a violent reaction to form elemental thallium as described above.

Figure 6: Background corrected synchrotron powder diffraction patterns (Hasylab, beamline B2, $\lambda = 0.47211 \text{ \AA}$, OBI detector system, capillary $\varnothing 0.3 \text{ mm}$) of TIHADC upon heating (patterns recorded between 180 and 300°C have been omitted). As a guide for the eye the theoretical patterns of TIHADC (blue) and Tl_2ADC (red) are shown as line diagrams.

It is surprising that the transformation from TIHADC to Tl_2ADC occurs quite smoothly in these experiments, whereas in the DTA/TG investigations a very violent decomposition reaction was observed (s. above). However, the temperatures for this decomposition obtained in the DTA/TG and diffraction experiments agree well with each other.

Tl₄(ADC)(oxa) was investigated in the temperature range 30°C to 270°C using 30°C steps. Tl₄(ADC)(oxa) is stable up to 120°C, a positive thermal expansion is observed for all lattice parameters. At 150°C Tl₄(ADC)(oxa) starts decomposing. Next to thallium in its high and room temperature modifications another compound is formed, which could not be identified up to now.

Conclusion

From aqueous solutions three new coordination polymers of thallium were obtained. Tl₂ADC and Tl₄(ADC)(oxa) crystallize in non-centrosymmetric space groups. This is probably caused by the influence of stereochemically active lone pairs at Tl(I). The crystal structure of TlHADC could not be solved up to now, due to twinning of the crystals we obtained. But its existence was corroborated by elemental analysis and its thermal behavior: upon heating TlHADC decomposes to form Tl₂ADC. Tl₂ADC decomposes at 195°C to form elemental thallium in its high and room temperature modifications, whereas Tl₄(ADC)(oxa) decomposes at approx. 150°C to form elemental thallium and another unknown compound.

As already mentioned Tl₄(ADC)(oxa) can be synthesized without adding oxalic acid (s. above). An explanation for this unusual behavior may be obtained from its crystal structure. In Figure 2 and Figure 4 it can be seen that in Tl₄(ADC)(oxa) and Tl₂ADC corrugated layers are formed by the Tl ions. Oxygen atoms of the carboxylates connect these Tl ions within the layers. The layers are then connected by the carboxylate dianions. In Tl₄(ADC)(oxa) every second ADC²⁻ anion of Tl₂ADC is replaced by an oxalate (s. Figure 4). Thus, in a very formal way, Tl₄(ADC)(oxa) can be obtained from Tl₂ADC by releasing two carbon atoms of every second ADC²⁻ anion. This reaction is indeed very unlikely, but in our ongoing experiments on coordination polymers using acetylenedicarboxylate as ligand we found that this ligand can be

oxidized at the C-C triple bond, if cations of noble metals are present. Thus the formed oxalate can then replace every second ADC^{2-} in the crystal structure of Tl_2ADC to form $\text{Tl}_4(\text{ADC})(\text{oxa})$. This reaction mechanism is still somewhat speculative and more experiments are necessary to corroborate these assumptions.

Acknowledgements

The help of the following people is greatly acknowledged: Dr. Ingo Pantenburg (University of Cologne) for help with X-ray single crystal data analysis, Prof. Ladislav Bohatý (University of Cologne) for SHG measurements, Dr. Klaus Müller-Buschbaum (LMU Munich) for DTA/TG measurements, and Heinrich Billetter (University of Cologne) for recording synchrotron powder diffraction data.

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Table 1: Details of single crystal structural analysis of Tl_2ADC and $\text{Tl}_4(\text{ADC})(\text{oxa})$.

	Tl_2ADC	$\text{Tl}_4(\text{ADC})(\text{oxa})$
Temperature	293 K	293 K
Formula	$\text{C}_4\text{O}_4\text{Tl}_2$	$\text{C}_6\text{O}_8\text{Tl}_4$
Molecular weight	$520.78 \text{ g}\cdot\text{mol}^{-1}$	$1017.54 \text{ g}\cdot\text{mol}^{-1}$
Space group	$P 2_1 2_1 2_1$ (No. 19)	$C 2$ (No. 5)
Diffractometer, radiation	Stoe IPDS-II, Mo- K_α	Stoe IPDS-II, Mo- K_α
Formula units Z	4	2
Unit cell	$a = 6.232(1) \text{ \AA}$ $b = 7.270(1) \text{ \AA}$ $c = 14.721(2) \text{ \AA}$	$a = 12.928(3) \text{ \AA}$ $b = 6.643(1) \text{ \AA}$ $c = 7.244(2) \text{ \AA}$ $\beta = 106.23(2)^\circ$
Volume	$667.0(1) \text{ \AA}^3$	$597.2(2) \text{ \AA}^3$
Density calculated	$5.186 \text{ g}\cdot\text{cm}^{-3}$	$5.658 \text{ g}\cdot\text{cm}^{-3}$
Crystal shape	Needle	Cuboid
Crystal size	$0.3 \text{ mm} \cdot 0.2 \text{ mm} \cdot 0.1 \text{ mm}$	$0.3 \text{ mm} \cdot 0.2 \text{ mm} \cdot 0.2 \text{ mm}$
Crystal color	Colorless	Colorless
h k l range		
$h_{\text{min/max}}$	-8 / 8	-17 / 17
$k_{\text{min/max}}$	-8 / 10	-9 / 9
$l_{\text{min/max}}$	-20 / 20	-10 / 10
$2\theta_{\text{max}}$	59.5°	59.5°
Number of reflections:		
measured	13099	5877
independent	1863	1657
μ	48.204 mm^{-1}	53.824 mm^{-1}
R-factors:		
$I_0 > 2\sigma(I_0)$	$R1 = 0.0568$; $wR2 = 0.1424$	$R1 = 0.0332$; $wR2 = 0.0800$
all data	$R1 = 0.0584$; $wR2 = 0.1444$	$R1 = 0.0389$; $wR2 = 0.0854$
R_{int}	0.1776	0.0796
GooF = S_{all}	1.095	1.077
Number of refined parameters	92	85
F(000)	872	848
Flack x	0.00(5)	0.67(4)*
$\Delta\rho_{\text{max}} / \Delta\rho_{\text{min}}$	$4.900 \text{ e}\cdot\text{\AA}^{-3} / -4.868 \text{ e}\cdot\text{\AA}^{-3}$	$1.765 \text{ e}\cdot\text{\AA}^{-3} / -1.524 \text{ e}\cdot\text{\AA}^{-3}$

* Inversion twin

Table 2: Selected interatomic distances [$\text{\AA}$] and angles [$^\circ$] in Ti_2ADC and $\text{Ti}_4(\text{ADC})(\text{oxa})$.

Ti_2ADC			
Ti1 - O11	2.756(13)	O11 - C1 - O12	126(1)
- O42	2.766(11)		
- O42	2.856(12)		
- O12	2.894(12)		
- O41	2.945(14)		
- O11	2.99(2)		
- O12	3.271(13)		
Ti2 - O42	2.635(11)	C1 - C2 - C3	179(2)
- O11	2.71(2)		
- O12	2.762(14)		
- O41	3.000(12)		
- O41	3.014(13)		
- O12	3.689(13)		
C1 - O12	1.23(2)	C2 - C3 - C4	175(2)
- O11	1.27(2)		
C4 - O42	1.25(2)	O41 - C4 - O42	127(1)
- O41	1.26(2)		
C1 - C2	1.45(2)		
C2 - C3	1.19(2)		
C3 - C4	1.50(2)		
$\text{Ti}_4(\text{ADC})(\text{oxa})$			
Ti1 - O31	2.673(12)	O11 - C1 - O12	121(1)
- O11	2.712(11)		
- O41	2.725(12)		
- O12	2.843(11)		
- O12	2.918(11)		
- O41	3.387(11)		
Ti2 - O41	2.572(12)	C1 - C2 - C2	175(1)
- O31	2.696(12)		
- O11	2.878(10)		
- O11	2.902(10)		
- O12	3.005(14)		
- O41	3.292(13)		
C1 - O11	1.27(2)	O31 - C3 - O31	126.1(9)
- O12	1.27(2)		
C3 - O31	1.234(13)	O41 - C4 - O41	123.2(8)

C4 - O41	1.28(2)
C1 - C2	1.42(2)
C2 - C2	1.23(2)
C3 - C4	1.56(2)

Figure 1: ORTEP diagrams of the coordination spheres around Tl1 (left) and Tl2 (right) in Tl₂ADC showing 50% probability thermal ellipsoids and the atom-numbering scheme. Tl-O bonds are drawn as broken lines.

Figure 2: Packing diagram of Tl₂ADC in a projection along [100] (Tl: large blue spheres, O: small red spheres, C: small white spheres). Tl-O bonds are drawn as broken lines.

Figure 3: ORTEP diagrams of the coordination spheres around Tl1 (left) and Tl2 (right) in Tl₄(ADC)(oxa) showing 50% probability thermal ellipsoids and the atom-numbering scheme. Tl-O bonds are drawn as broken lines.

Figure 4: Packing diagram of Tl₄(ADC)(oxa) in a projection along [010] (Tl: large blue spheres, O: small red spheres, C: small white spheres). Tl-O bonds are drawn as broken lines.

Figure 5: Synchrotron powder diffraction pattern (Hasylab, beamline B2, $\lambda = 0.47211 \text{ \AA}$, OBI detector system, capillary $\varnothing 0.3 \text{ mm}$) of the residue of Tl₂ADC after heating at 240°C showing the observed (+) and calculated patterns (solid line) as well as the difference between them. Vertical bars mark the positions of the reflections of HT-Thallium (lower bars) and RT-Thallium (upper bars).

Figure 6: Background corrected synchrotron powder diffraction patterns (Hasylab, beamline B2, $\lambda = 0.47211 \text{ \AA}$, OBI detector system, capillary $\varnothing 0.3 \text{ mm}$) of TIHADC upon heating (patterns recorded between 180 and 300°C have been omitted). As a guide for the eye the theoretical patterns of TIHADC (blue) and Tl₂ADC (red) are shown as line diagrams.

Graphical Abstract

Non-centrosymmetric Coordination Polymers Based On Thallium and Acetylenedicarboxylate

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