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Uwe Ruschewitz, Ruth Ahlers. [Tl₂Zn(ADC)₂(H₂O)₂]: the first coordination polymer with acetylenedicarboxylate (ADC²⁻) as bridging ligand containing two different metal ions. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2009, 636 (1), pp.11. <10.1002/zaac.200900428>. <hal-00533402>

HAL Id: hal-00533402

<https://hal.science/hal-00533402v1>

Submitted on 6 Nov 2010

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Zeitschrift für Anorganische und
Allgemeine Chemie

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Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.200900428
Wiley - Manuscript type:	Communication
Date Submitted by the Author:	06-Sep-2009
Complete List of Authors:	Ruschewitz, Uwe; Universitaet zu Koeln, Department fuer Chemie Ahlers, Ruth; Universitaet zu Koeln, Department fuer Chemie
Keywords:	Acetylenedicarboxylate, Coordination Polymer, Crystal Structure, Thallium, Zinc



SHORT COMMUNICATION

DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

 ∞^3 [Tl₂Zn(ADC)₂(H₂O)₂]: the first coordination polymer with acetylenedicarboxylate (ADC²⁻) as bridging ligand containing two different metal ionsRuth Ahlers^[a] and Uwe Ruschewitz*^[a]Dedicated to Prof. Arndt Simon on the Occasion of his 70th birthday.**Keywords:** Acetylenedicarboxylate; Coordination Polymers; Crystal Structure; Thallium; Zinc

From an aqueous solution containing ZnCO₃, Tl(CH₃COO), and acetylenedicarboxylic acid (H₂ADC: HOOC-C≡C-COOH) single crystals of ∞^3 [Tl₂Zn(ADC)₂(H₂O)₂] (**1**) were obtained. **1** crystallizes in triclinic space group P $\bar{1}$ with Z = 1. A slightly distorted octahedral ZnO₆ coordination and a very unsymmetric TlO₆ coordination (Tl-O < 321 pm) are found, the latter probably

being caused by a stereochemically active lone pair at Tl⁺. These polyhedra are connected by the ADC²⁻ linker to form a 3D network structure. Additionally, hydrogen bonds are formed, which involve the water molecules (O[⋯]O starting at 274 pm). These are only coordinated to Zn²⁺. **1** is the first coordination polymer of ADC²⁻, which contains two different metal ions.

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Introduction

Coordination polymers, especially their porous exponents frequently named MOFs (metal-organic framework) [1], are in the focus of many research groups world-wide. Their easy synthetic accessibility as well as their potential applications [2] have mainly caused this interest. But also the perspective to construct or even to “design” new solids starting from simple building blocks like metal ions or metal-oxo clusters and organic polyfunctional ligands [3] is attractive and another reason for the ongoing interest in coordination polymers. But, despite some spectacular achievements [4], the real design, i.e. the synthesis of a new coordination polymer with an *a priori* given structural arrangement is in most cases difficult or even impossible.

In our work we have mainly concentrated on acetylenedicarboxylate (ADC²⁻), as this is one of the simplest linker, which can be used for the synthesis of coordination polymers. It consists of a rigid carbon backbone with two coordinating carboxylate groups. Thus, it is predestined to investigate the underlying mechanisms and interactions that lead to the formation of a specific structural arrangement. The first coordination compounds with ADC²⁻ were published by Robl [5]. In recent years we have been able to synthesize several hydrous [6] and anhydrous [7] coordination polymers with ADC²⁻ as bridging ligand, as well as compounds with pyridine or 4,4'-bipyridine as additional ligand [8]. Very recently it was shown that ADC²⁻ can also be used to synthesize MOF-type coordination polymers [9]. In this work we will present the first coordination polymer with ADC²⁻ that contains two different metal ions, namely Tl⁺ and Zn²⁺.

Results and Discussion

∞^3 [Tl₂Zn(ADC)₂(H₂O)₂] (**1**) crystallizes in triclinic space group P $\bar{1}$ (no. 2) with Z = 1. ORTEP diagrams of the coordination spheres around Zn²⁺ and Tl⁺ are shown in Figure 1, some selected interatomic distances and angles are given in Table 2. For Zn²⁺, a slightly distorted octahedral coordination is found, formed by four oxygen atoms of four different ADC²⁻ ligands and two oxygen atoms of two water molecules. The Zn-O distances to oxygen atoms of the water molecules (O5) are distinctively shorter than those to oxygen atoms of the ADC²⁻ ligands (s. Table 2). But they are in the range found for ∞^3 [Zn(ADC)(H₂O)₂] [6f] (Zn-O = 206.7 – 215.1 pm), which also exhibits a slightly distorted octahedral ZnO₆ coordination with two water molecules in *trans* positions.

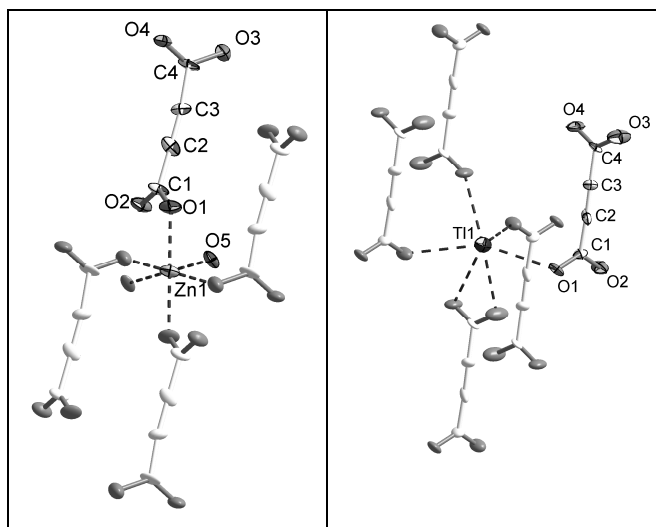


Figure 1. ORTEP diagrams of the coordination spheres around Zn (left) and Tl (right) in ∞^3 [Tl₂Zn(ADC)₂(H₂O)₂] (**1**) showing 50% probability thermal ellipsoids and the atom-numbering scheme. Zn-O and Tl-O bonds are drawn as broken lines.

The coordination sphere around Tl^+ is less symmetric. Using the formalism of Brese and O’Keeffe [10], a valence $v_i = 0.79$ is calculated taking into account six Tl-O distances < 321 pm. Adding two next-nearest neighbour distances given in Table 2, the valence is only slightly increased ($v_i = 0.84$) so that only six nearest neighbour distances with Tl-O < 321 pm will be considered in the following. These oxygen atoms belong to five different ADC^{2-} ligands with one carboxylate group coordinating in a chelating mode. The coordination sphere of Tl^+ is shown in Figure 1 (right). Apparently, one hemisphere of its coordination sphere is unoccupied, obviously accommodating a stereochemically active lone pair of Tl^+ . Similar results were obtained for Tl_2ADC [7e], also the Tl-O distances are very similar in both compounds (Tl_2ADC : Tl-O = 263.5 – 327.1 pm). It is noteworthy that the water molecule (O5) is not part of the inner coordination sphere of Tl^+ (Tl-O5 = 360 pm). It is coordinating only to Zn^{2+} .

With respect to ADC^{2-} O1 coordinates to Tl and Zn, O2 to two Tl atoms. Carboxylate group O3-C4-O4 coordinates in a four-dentate mode bridging two Tl – one in a chelating mode – and one Zn atom. The distances and angles within the ADC^{2-} ligand are in the expected range, although the accuracy of these values is modest due to the high scattering power of Tl.

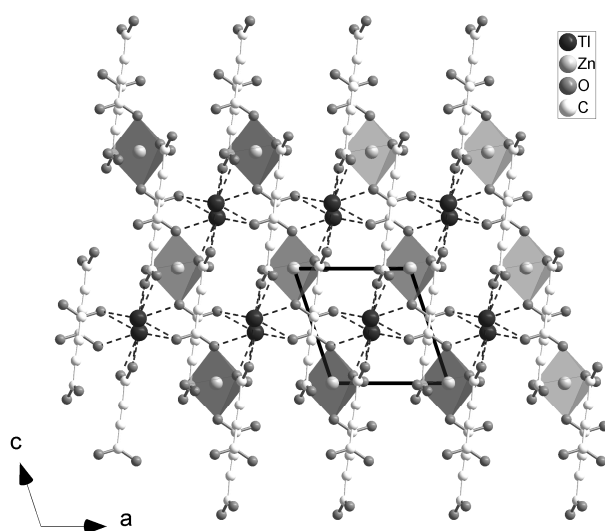


Figure 2. Packing diagram of ${}^3[\text{Tl}_2\text{Zn}(\text{ADC})_2(\text{H}_2\text{O})_2]$ (**1**) in a projection along [010]. ZnO_6 octahedra are emphasized and Tl-O bonds are drawn as broken lines.

The packing diagram of the crystal structure of **1** is shown in Figure 2. Tl and Zn atoms are connected by the ADC^{2-} ligands to form a 3D network structure. Additionally, hydrogen bonds are formed between water molecule O5 and oxygen atoms of the carboxylate groups ($\text{O5} \cdots \text{O} = 274 - 284$ pm). Also small channels parallel to [010] can be seen in Figure 2. These channels are not empty; most likely they accommodate the lone pair of Tl^+ .

In an alternative description the crystal structure of **1** can be understood as consisting of ${}^1[\text{Zn}(\text{ADC})_{4/2}(\text{H}_2\text{O})_2]^{2-}$ chains, which are connected by Tl^+ ions to form a 3D network structure.

Table 1. Details of single crystal structural analysis of ${}^3[\text{Tl}_2\text{Zn}(\text{ADC})_2(\text{H}_2\text{O})_2]$ (**1**).

${}^3[\text{Tl}_2\text{Zn}(\text{ADC})_2(\text{H}_2\text{O})_2]$ (1)	
Formula	C8H4O10Tl2Zn
Crystal size	0.2 x 0.2 x 0.2 mm
Crystal color	Colorless
Diffractometer, λ	Stoe IPDS I, 71.073 pm
Temperature	293 K
Space group; Z	$P\bar{1}$, 1
Unit cell	a = 728.9(2) pm b = 737.6(2) pm c = 751.1(2) pm $\alpha = 113.18(3)^\circ$ $\beta = 95.22(3)^\circ$ $\gamma = 115.55(3)^\circ$
Volume	0.3179(2) nm ³
Density calculated	3.835 Mg/m ³
$2\theta_{\text{max}}$	56.4°
Number of reflections:	
independent	1422
$F^2 > 2\sigma(F^2)$	879
μ/mm^{-1}	27.20 mm ⁻¹
R1 ($F^2 > 2\sigma(F^2)$)	0.074
wR2 (all data)	0.196
Goof	0.93
Number of refined parameters	97
$\Delta\rho_{\text{min/max}}$	-3.01 pm ⁻³ / 3.41 pm ⁻³

Table 2. Selected interatomic distances (pm) and angles (°) in ${}^3[\text{Tl}_2\text{Zn}(\text{ADC})_2(\text{H}_2\text{O})_2]$ (**1**).

Tl1 – O3	270(2)	C1 – O1	126(3)
– O1	288(2)	C1 – O2	121(2)
– O2	292(2)	C4 – O3	127(3)
– O4	300(2)	C4 – O4	122(3)
– O2	301(2)		
– O4	321(1)	C1 – C2	143(3)
– O1	354(2)	C2 – C3	124(3)
– O5	360(2)	C3 – C4	146(3)
Zn1 – O5	204(1) 2x		
– O3	211(3) 2x		
– O1	213(2) 2x		
O1 – Zn1 – O3	94.2(7) 2x	O1 – C1 – C2	115(2)
O1 – Zn1 – O5	94.0(6) 2x	O2 – C1 – C2	117(2)
O3 – Zn1 – O5	95.9(6) 2x	O3 – C4 – C3	118(2)
		O4 – C4 – C3	118(2)
O1 – C1 – O2	128(2)	C1 – C2 – C3	178(2)
O3 – C4 – O4	124(2)	C2 – C3 – C4	174(2)

Conclusions

In summary, we have been able to synthesize the first example of a coordination polymer with ADC^{2-} as bridging ligand that contains two different metal ions, namely Tl^+ and Zn^{2+} . The synthesis of such compounds is not straightforward, as in most cases the formation of “binary” (i.e. one metal and one bridging ligand) compounds or a mixture of both – here: Tl_2ADC [7e] and ${}^3[\text{Zn}(\text{ADC})(\text{H}_2\text{O})_2]$ [6f] – is preferred. That means, the synthetic conditions (solvent,

temperature etc.) have to be adjusted such that the ternary compound crystallizes before the crystallization of the possible binary products starts. To our knowledge the synthesis of such ternary coordination polymers is not reported very often compared to numerous examples of binary compounds. Especially the synthesis of ternary porous coordination polymers seems to be worthwhile, as they should offer a great potential as ion exchanger.

It was observed that compounds containing a stereochemically active lone pair show an enhanced probability to crystallize in acentric space groups [11]. Actually, Ti_2ADC [7e], [12] and $\text{Ti}_4(\text{ADC})(\text{oxa})$ (oxa = oxalate) [7e)] were found to crystallize in acentric space groups, while $[\text{Ti}_2\text{Zn}(\text{ADC})_2(\text{H}_2\text{O})_2]$ (**1**) crystallizes in centrosymmetric space group $\text{P}\bar{1}$. Therefore more examples of coordination polymers with Ti^+ are necessary to evaluate the applicability of this observation.

Experimental Section

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

Synthesis.

$[\text{Ti}_2\text{Zn}(\text{ADC})_2(\text{H}_2\text{O})_2]$ (**1**): In a beaker 0.063 g (0.5 mmol) ZnCO_3 , 0.263 g (1 mmol) $\text{Ti}(\text{CH}_3\text{COO})$ and 0.114 g (1 mmol) H_2ADC were dissolved in 4 mL demineralized water. The beaker was sealed with a perforated foil. After evaporation of the solvent at room temperature (approx. 8 days) colorless crystals precipitated, from which a single crystal suitable for a structure analysis was isolated. According to X-ray powder diffraction data (Huber G 670, $\text{CuK}\alpha_1$ radiation) the sample is single-phase.

X-ray single-crystal structure analysis.

Single crystals of **1** were isolated from the precipitate as described above and mounted in sealed glass capillary on a Stoe IPDS I single-crystal diffractometer ($T \approx 293$ K, $\text{MoK}\alpha$ radiation). For data collection and reduction the Stoe program package [13] was applied. The structural model was solved using SIR-92 [14] and completed using difference Fourier maps calculated with SHELXL-97 [15], which was also used for final refinement. All programs were run under the WinGX system [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the water molecule could not be located in the Fourier map and were therefore not included in the final refinement. More details of the structural analysis [17] are given in Table 1. Selected interatomic distances and angles are listed in Table 2.

Acknowledgments

We would like to thank Dr. Ingo Pantenburg and Ingrid Müller for collecting single-crystal X-ray diffraction data.

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- [17] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-746532. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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