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Short communication

Azulene-1-carboxylate - A new azulene-based building block for coordination polymers $\stackrel{\star}{\sim}$



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G R A P H I C A L A B S T R A C T

New crystalline coordination polymers have been constructed using for the first time the azulene-1-carboxylate anion as building block.



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ABSTRACT

For the first time, the easily accessible azulene-1-carboxylate anion has been employed as building block for the construction of crystalline coordination polymers. Neutralization of azulene-1-carboxylic acid (3) with NaOH in aqueous solution provided the dark purple sodium salt $C_{10}H_7CO_2Na H_2O$ (4) in 85% isolated yield. Single-crystal X-ray diffraction of 4 revealed a supramolecular layer structure in the crystalline state. Subsequent treatment of 4 with 1 equiv. of Me₃SnCl afforded a rare organotin derivative of azulene, namely polymeric $[C_{10}H_7CO_2SnMe_3]_n$ (5) as purple crystals (82% yield).

Azulene ($C_{10}H_8$, **1**, *cf.* Scheme 1) has fascinated chemists for many decades due to its unusual electronic properties as well as its unique royal-blue color [1,2]. Potential practical applications of azulene and derivatives thereof include advanced electrochromic materials [3,4], optoelectronics [5,6], liquid crystal displays [7], and the manufacture of cosmetics [8]. There are only limited studies on polymeric or supramolecular assemblies based on azulene. Prominent examples are *e.g.* supramolecular complexes of calix[4] azulenes [9–11], azulene-based spacers in one-dimensional coordination polymers [12], as well as a number of π - π -bonded dimers [13–16].

We report here the first-time use of the readily accessible azulene-1-carboxylate anion in the synthesis of crystalline coordination polymers, including a rare example of an azulene organotin derivative [17,18]. The synthetic protocol leading to the title compounds is outlined in Scheme 1. Treatment of the parent azulene 1 [19] with trifluoroacetic anhydride (TFAA) in dichloromethane solution according to a published procedure [20] afforded 1-trifluoroacetylazulene 2 in

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^{*} Dedicated to Professor Dieter Kaufmann on the occasion of his 70th birthday.

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Scheme 1. Bottom-up synthesis of the title compounds 4 and 5 (TFAA = trifluoroacetic anhydride) starting from azulene (1) [21,22].



Fig. 2. a,b. Polymeric ladder structure of **4** in the crystal (a); Association of the ladders to supramolecular layers by $C_2^{-1}(4)$ -type O-H···O hydrogen bonds. The hydrogen-bonded O···O distances are 276.3(2) and 283.6(2) pm, and the H···O separations are estimated at 182(2) and 192(2) pm.

high yield. Hydrolysis using aqueous NaOH followed by acidification provided the starting material azulene-1-carboxylic acid (**3**, also named 1-azuloic acid) as a lavender, microcrystalline solid [20]. Surprisingly, no well-defined simple alkali metal salts have been reported in the previous literature. We found that such salts are easily accessible by neutralization of **3** with alkali metal hydroxides (MOH, M = Li-Cs) in aqueous solutions. In all cases, dark purple solutions of the alkali metal azulene-1-carboxylates were formed, but only in the case of sodium the reaction product $C_{10}H_7CO_2Na$ could be isolated as a dark purple, crystalline hydrate $C_{10}H_7CO_2Na$ ·H₂O (4) in 85% yield [21]. Especially in the case of M = Rb and Cs, all crystallization attempts led to formation of insoluble decomposition products. Finally, a novel organotin derivative of **3** could be prepared by treatment of sodium salt **4** with 1 equiv. of trimethyltin chloride in aqueous solution affording a purple



Fig. 3. Asymmetric unit of compound **5** in the crystal. Displacement ellipsoids drawn at the 50% probability level, symmetry-equivalent atoms are semi-transparent. Selected bond lengths [pm] and angles [°]: Sn-O₁ 218.5(1), Sn-O₂' 232.2(1), Sn-C12 211.4(2), Sn-C13 211.9(2), Sn-C14 211.7(2), O₁-Sn-O₂' 172.87(5), C12-Sn-C13 119.81(8), C12-Sn-C14 124.22(9), C13-Sn-C14 115.56(9), Sn-O₁-C11 128.4(1), Sn"-O₂-C11 142.4(1), C11-O₁ 127.3(2), C11-O₂ 125.0(2), C1-C11 147.1(2), O₁-C11-O₂ 122.4(2).

precipitate in 82% isolated yield, which could be identified as polymeric $[C_{10}H_7CO_2SnMe_3]_n$ (5) (*cf.* Scheme 1).

The new compounds **4** and **5** were fully characterized in a straightforward manner through their IR and NMR spectra as well as elemental analyses. The ¹H and ¹³C NMR of both compounds were readily interpretable and in good agreement with the expected formulation. In the IR spectrum of **4**, bands attributable to the carbonyl group were observed at 1576 (ν_{as} C=O) and 1537 (ν_s C=O) cm⁻¹. The high purity of the organotin derivative **5** was indicated by a single resonance ($\delta = 58.2$ ppm) in the ¹¹⁹Sn NMR spectrum.

The molecular and crystal structures of **2–5** have all been determined by single-crystal X-ray diffraction [23]. Surprisingly, the crystal structures of the long-known 1-trifluoroacetylazulene (**2**) and azulene-1-carboxylic acid (**3**) had not been determined before. Dark red, needle-like single-crystals of **2** and **3** were obtained by slow evaporation of saturated solutions in acetone. The crystal structure of **2** contains monomeric molecules, while in **3** hydrogen-bonded dimers comprising a central eight-membered ring with two O–H…O hydrogen bonds (graph set $R_2^{-2}(8)$ [24]) are present (*cf.* Figs. S2–S7 in the SI). In

both **2** and **3**, the molecules are further aggregated to chain-like assemblies by π - π -stacking interactions between parallel-oriented azulenyl moieties. The closest C··C separations are 340.8(2) pm (**2**) and 335.1(2) pm (**3**).

The main goal of the present study was to utilize the azulene-1-carboxylate anion as a new building block for crystalline coordination polymers. This was achieved by structurally characterizing the new compounds **4** and **5** which both exhibit remarkable macromolecular structures in the crystalline state. Well-formed, dark purple, needle-like single-crystals of **4** (*cf.* Fig. 1a) were grown by slow evaporation of an aqueous solution. Fig. 1b depicts the asymmetric unit in the crystal structure of **4**.

The carboxylate moiety adopts a μ_3 -bridging $\kappa O, O': \kappa O: \kappa O$ coordination, and the sodium atom displays an irregular penta-coordination which is completed by one H₂O ligand. The interconnection of sodium atoms by azulene-1-carboxylate ligands results in a ladderlike polymeric structure, being composed of edge-shared Na₂O₂ rings (Fig. 2, a). This arrangement might be supported by π - π -stacking interactions between the parallel-arranged azulene backbones. However, the closest C···C contact between neighbored azulen-1-yl groups is 350.8(2) pm and therefore considerably larger than the values observed for **2** and **3**. The polymeric ladders in **4** are further interconnected by O–H···O hydrogen bonds between H₂O ligands and one of the carboxylate oxygens (O2), displaying a chain-like pattern which can be described by the graph set $C_2^{-1}(4)$ [24]. The result is a supramolecular layer structure with the azulene backbones situated at the surface (Fig. 2, b).

Purple, needle-like single crystals of the organotin derivative **5** were obtained by slow cooling a saturated solution in acetone to r.t. Despite the preparation in aqueous solution, the compound does not contain coordinated water molecules or water of crystallization. The coordination of the carboxylate group is simpler than in the sodium derivative **4**, being a μ -bridging $\kappa O:\kappa O'$ mode (Fig. 3). The tin atom displays a typical trigonal-bipyramidal coordination, with two carboxylate oxygen atoms occupying the axial positions. Consequently, the molecular structure of **5** is a polymeric chain composed of alternating trimethyltin and azulene-1-carboxylate building blocks (Fig. 4). Supramolecular interactions between the chains have not been observed, and the azulene-1-yl groups are not properly oriented for efficient π - π stacking.

In summarizing the results reported here, we successfully established the readily accessible azulene-1-carboxylate anion as a new building block for crystalline coordination polymers. The dark-purple sodium salt $C_{10}H_7CO_2Na\cdot H_2O$ (4) features a supramolecular layer structure in the crystalline state, containing polymeric ladders which



Fig. 4. Polymeric chain structure of 5 in the crystalline state (coordination polyhedra around the tin atoms highlighted in purple). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

are linked by $O-H\cdots O$ hydrogen bonds. Treatment of **4** with 1 equiv. of trimethyltin chloride allowed for the synthesis of a rare organotin derivative of azulene, $[C_{10}H_7CO_2SnMe_3]_n$ (5), being a chain-like coordination polymer.

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Appendix A. Supplementary material

Crystallographic data for the crystal structures reported in this paper can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; URL: http://www.ccdc.cam.ac.uk/) by referring to the depository numbers CCDC 1850261 (2), 1850308 (3), 1850262 (4), and 1850260 (5). Supplementary data to this article can be found online at doi:https://doi.org/10.1016/j. inoche.2018.11.021.

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- [21] Synthesis of sodium azulene-1-carboxylate (4): 2.0 g (11.6 mmol) azulene-1carboxylic acid (3) was suspended in water (50 mL) and neutralized with the calculated amount of NaOH (0.46 g, 11.6 mmol), dissolved in 10 mL water. The resulting purple solution was filtered to remove a small amount of brown, insoluble material. Slow evaporation in air produced dark purple, needle-like crystals of 4 in high yield (1.92 g, 85%). C11H7NaO2 (194.17 g/mol): calcd.: C, 68.05; H, 3.63%; found: 67.58; H, 3.60%. ¹H NMR (296 K, D₂O, 400 MHz): $\delta = 9.26$ (d, 1H, H8, J = 9.6 Hz), 8.33 (d, 1H, H4, ${}^{3}J = 9.6$ Hz), 8.13 (d, 1H, H2, ${}^{3}J = 3.8$ Hz), 7.65 (t, 1H, H6), 7.29 (t, 1H, H7), 7.25, 7.20 (t, 1H, H5; d, 1H, H3, superimposed). ¹³C NMR $(296 \text{ K}, D_2O, 100 \text{ MHz}): \delta = 177.0 \text{ (C=O)}, 145.4 \text{ (C1O)}, 141.7 \text{ (C6)}, 141.2 \text{ (C2)},$ 140.7 (C9), 140.4 (C4), 139.4 (C8), 128.2 (C7), 128.0 (C5), 125.7 (C1), 118.8 (C3). IR (ATR): $\nu_{max} = 3424$ (m), 3296 (m), 3095 (w) (ν CH), 3079 (w) (ν CH), 3051 (w) (ν CH), 2993 (w) (ν CH), 1683 (w), 1631 (w), 1576 (m) (ν_{as} C=O), 1537 (m) (ν_{s} C=O), 1495 (s), 1460 (s), 1436 (s), 1414 (s), 1393 (s), 1364 (s), 1300 (m), 1284 (s), 1217 (m), 1155 (m), 1045 (m), 1005 (m), 977 (w), 942 (w), 921 (w), 879 (w), 822 (w), 802 (m), 771 (m), 732 (m), 714 (m), 685 (w), 629 (w), 612 (m), 540 (m), 512 (s), 498 (s), 404 (m), 382 (m), 315 (m), 276 (m), 207 (m), 193 (m), 183 (m), 164 (m), 115 (m), 83 (s), 71 (m), 65 (s), 57 (m) cm⁻
- [22] Synthesis of trimethyltin azulene-1-carboxylate (5): Sodium salt 4 was prepared as described above from 2.0 g (11.6 mmol) azulene-1-carboxylic acid (3) in 50 mL water. A solution of 2.32 g (11.6 mmol) Me₃SnCl (*Careful! Me₃SnCl is toxic and must be handled only under a well-ventilated fume hood!*) in 20 mL of warm (30–40 °C) water is added under rapid stirring to produce a purple precipitate of 5. After stirring for another 10 min, the precipitate is isolated by filtration through a glass filter and dried in air. Recrystallization from a minimum amount of acetone afforded purple, needle-like crystals of pure 5 in 82% isolated yield (3.19 g). $C_{14}H_{16}O_{2}Sn$ (334.99 g/mol): calcd.: C, 50.20; H, 4.81%; found: 49.80; H, 4.66%. ¹H NMR (600.1 MHz, acetone- d_6 , 20 °C): δ = 9.73 (d, 1H, *J* = 9.1 Hz, H8), 8.55 (d, 1H, *J* = 10.6 Hz, H4), 8.33 (d, 1H, H2), 7.86 (t, 1H, H6), 7.54 (t, 1H, H7), 7.48 (t, 1H, H5), 7.32 (d, 1H, H3), 0.59 (s, 9H, CH₃) ppm. ¹³C NMR (150.9 MHz, acetone- d_6 , 20 °C): δ = 170.3 (C=0), 145.1 (C10), 139.6 (C6), 140.8 (C9), 141.7 (C2), 138.9 (C4), 138.7 (C8), 127.3 (C7), 126.9 (C5), 121.1 (C1), 117.6 (C3), -1.0 (CH₃) ppm. ¹¹⁹Sn (149.2 MHz, acetone- d_6 , 20 °C): δ = 58.2 ppm.
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