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An Unusual 3D Zinc-Organic Framework Constructed from Paddle-Wheel-Based Carboxylate Sheets Bridged by Acetate Ions

Nathalie Saffon-Merceron,^[a] Marie-Claire Barthélémy,^[c] Christophe Laurent,^[c] Isabelle Fabing,^[b] Pascal Hoffmann,^{*[b]} and Alain Vigroux^{*[b]}

Keywords: Metal-organic frameworks; 2,6-Naphthalenedicarboxylate; Zinc; Paddle-wheel MOF; Bridging acetate ligand; Super-critical CO₂ activation

Abstract. A zinc-2,6-naphthalenedicarboxylate metal-organic framework, (H₂NEt₂)[Zn₂(AcO)(NDC)₂]*n*DEF (**1**) (DEF = *N,N*-diethylformamide, AcO = acetate), was solvothermally synthesized in the presence of small amounts of acetic acid and characterized by single-crystal and powder X-ray diffraction and thermogravimetric analysis. Compound **1** is an anionic 3D paddle-wheel MOF, in which the zinc-naphthalenedicarboxylate sheets are linked together by bridging acetate ions.

Compound **1** exhibits large square channels (13 × 13 Å), which contain DEF molecules and, alternatively, charge-balancing diethylammonium cations in situ generated by the hydrolysis of DEF under the solvothermal conditions used. The anionic host framework of **1** is unstable upon removal of guest DEF molecules suggesting that host-guest hydrogen bond interactions are crucial for maintaining the structural integrity of this compound.

Introduction

Crystalline metal-organic frameworks (MOFs) have attracted considerable attention during the last decade largely because they have significantly expanded the potential capabilities of classically porous materials such as zeolites, metal oxides, or activated carbons.^[1] MOFs are constructed by joining metal-containing units, referred to as secondary building units (SBUs), with organic linkers. The modular assembly of a large variety of metal SBUs and organic linkers has led to more than 20,000 different MOFs being reported and characterized within the past decade.^[2] The hybrid nature of MOFs thus provides a wealth of opportunities for discovering intriguing and fascinating new structures and, more importantly, for engineering new functional materials for a wide range of potential uses including catalysis, separation, gas storage, and drug delivery.^[3]

One of the most common SBUs formed by metals and carboxylates is the square $M_2(O_2CR)_4$ paddle-wheel unit, in which two metal atoms are bridged by four carboxylates in *syn-syn*

mode.^[4,5] These paddle-wheel units can be linked into two-dimensional (2D) networks using linear dicarboxylates. In this case, the axial sites of the SBU are either unoccupied or coordinated to terminal capping ligands, typically monodentate neutral molecules. This type of arrangement, in which the paddle-wheel SBU acts as a square planar node (with four points of extension) has been observed with many different metal atoms in a vast number of 2D carboxylate MOFs, although zinc and copper are by far the most frequently encountered metals. The square $M_2(O_2CR)_4$ paddle-wheel units can also be linked into 3D frameworks by using, in addition to linear dicarboxylate linkers, bidentate neutral molecules (typically linear ditopic nitrogen donors). In this case, the paddle-wheel SBU acts as a six-connecting (octahedral) structural unit, in which the axial sites are occupied by the bidentate neutral ligands acting as pillaring agents, thus extending the 2D metal-dicarboxylate layers into 3D structures. As far as it is known, 2D metal-dicarboxylate sheets have never been reported to link into a 3D framework unless neutral pillaring ligands are present in the reaction mixture. Herein, the synthesis, structural characterization, and stability of an unprecedented anionic 3D paddle-wheel-based MOF of formula unit (H₂NEt₂)[Zn₂(AcO)(NDC)₂] (**1**), constructed from the linkage of zinc-2,6-naphthalenedicarboxylate (Zn-NDC) layers through axially coordinated acetate ions are reported.

Results and Discussion

The extensively studied Zn-aromatic dicarboxylic acid-DEF system (DEF = *N,N*-diethylformamide) are further explored for the purpose of discovering new zinc-dicarboxylate MOF structures based on commercially available linear dicarboxylate lin-

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kers. The synthesis of zinc-dicarboxylate MOFs is frequently performed by heating a mixture of aromatic dicarboxylic acid and zinc(II) nitrate, typically in its hexahydrate or tetrahydrate form, in a system solvent that usually contains *N,N*-diethylformamide (DEF) or *N,N*-dimethylformamide (DMF). This procedure, when carefully applied to a wide variety of rigid and linear dicarboxylic acids, reliably produces large single crystals of isorecticular MOFs (IRMOFs), which consist of Zn_4O units connected by the dicarboxylate struts to form a common cubic topology. IRMOF-1 of formula $Zn_4O(BDC)_3$ (BDC = 1,4-benzenedicarboxylate), originally named MOF-5,^[6] and IRMOF-8 of formula $Zn_4O(NDC)_3$ (NDC = 2,6-naphthalenedicarboxylate) are two representative structures of this series prepared under common solvothermal conditions.^[7] Recently, the effect of adding small amounts of formic acid under the MOF-5 synthesis conditions was explored and the formation of new Zn-BDC MOF structures was discovered.^[8] With the aim of discovering new Zn-NDC based MOFs, the phase selection effect that small amounts of added acetic acid might exert on the NDC-Zn system under solvent and reaction conditions previously described for the preparation of IRMOF-8 was similarly investigated.^[7,9–11]

Synthesis of $(H_2NEt_2)[Zn_2(AcO)(NDC)_2] \cdot nDEF$ (**1**)

Initially, IRMOF-8 was synthesized using common solvothermal routes in DEF by varying metal:ligand ratios between 2 and 3.5, incubation times between 18 and 36 h, and temperature ranges between 80 and 130 °C.^[7,9,12] X-ray diffraction of the single crystals so obtained indicates that the material corresponds to doubly interpenetrated phases of either IRMOF-8 or its recently described analogues.^[9–12] When the latter syntheses were conducted in the presence of added acetic acid (10 equiv. relative to 2,6-naphthalenedicarboxylic acid), the corresponding IRMOF-8 crystals formed erratically during the heating period. However, within the temperature range of 80 to 130 °C, the absence of crystal formation during the first 5 h of heating was always noticed. It was therefore decided to limit the heating time to 5 h to prevent IRMOF-8 crystals from building up. By carrying out the reaction during 5 h at 130 °C, after cooling to room temperature the slow formation (5–10 d) of colorless needle-like crystals as the unique crystalline product was observed. Single-crystal and powder X-ray diffraction (PXRD) analyses (Figure 1) indicated that the framework **1** of formula $(H_2NEt_2)[Zn_2(AcO)(NDC)_2] \cdot nDEF$ was obtained. However, it should be noted that small reflections in addition to those expected for phase-pure **1** are observed in Figure 1. The latter are not consistent with the PXRD data of IRMOF-8^[9] and could well result from a partial degradation of the material under the conditions used for recording the PXRD patterns, probably via the adsorption of water molecules contained in the air.

Crystal Structure

Single-crystal X-ray diffraction measurements revealed that **1** crystallizes in the tetragonal space group $P4_2/mbc$. The

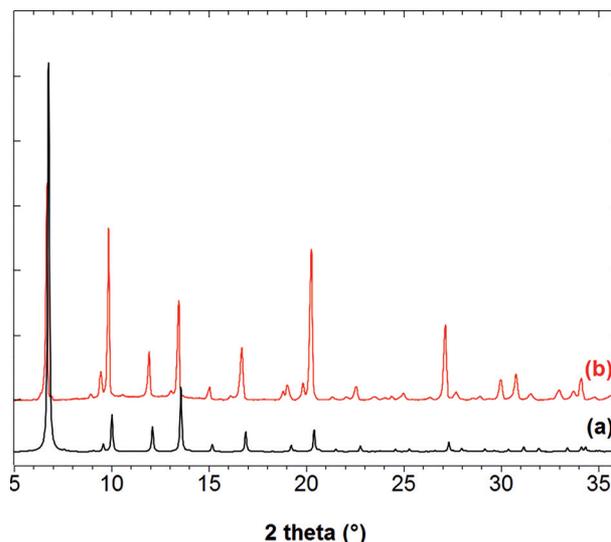


Figure 1. PXRD pattern simulated (1.54056 Å) from the single-crystal data of **1** (a), and measured (1.541874 Å) from a sample of **1** (b).

asymmetric unit consists of the $Zn(AcO)(NDC)$ motif and a disordered diethylammonium cation arising from the hydrolysis reaction of DEF. It is indeed well known that formamide-based solvents like DMF or DEF may undergo a significant degree of hydrolysis under solvothermal conditions depending on the initial water content [Equation (1)].



It has been shown that anionic MOFs having diethylammonium ions as counter-cations can arise either in partially hydrated DEF^[8,13] or in anhydrous DEF to which diethylammonium chloride had been added,^[13] suggesting that the diethylammonium cations (either added or resulting from the hydrolysis of DEF) play a templating role in the crystallization of anionic networks. Similarly, MOFs having dimethylammonium ions as counter-cations have been described as resulting from the hydrolysis reaction of DMF.^[13,14]

Compound **1** is constructed from dimeric zinc clusters with a typical paddle-wheel structure, which are interconnected by NDC dianions to form a perfect 2D square-grid parallel to the *ab* plane. The axial sites of the Zn_2 paddle-wheel units are occupied by acetate ions, which are tightly coordinated to the zinc with a Zn1–O5 distance of 1.95(5) Å. The acetate ions unexpectedly act as bridging agents, thus giving rise to infinite anionic chains along the *c* axis (Figure 2). As a result, a non-interpenetrated 3D anionic architecture with large square channels of approximate dimensions 13×13 Å is created (Figure 3). Within the infinite anionic chains, the two bridging oxygen atoms of acetates are alternatively oriented in opposite directions towards the charge-balancing diethylammonium cations. Consequently, the anionic framework of **1** exhibits channels that are alternatively occupied and unoccupied by the diethylammonium counter-cations (Figure 4).

Similarly to diethyl- or dimethylammonium cation, the formate ion derived from hydrolysis of DEF or DMF

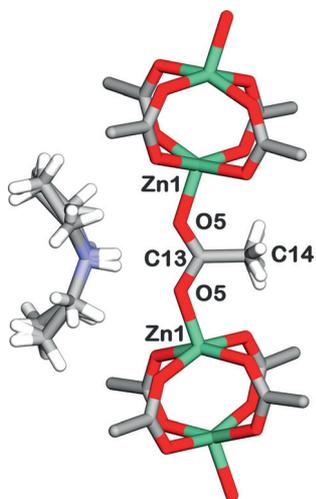


Figure 2. View of two adjacent paddle-wheel SBUs of **1** interconnected by an acetate ion and its (disordered) diethylammonium counter-cation (color code: Zn: green; C: gray; H: white; N: blue; O: red).

[Equation (1)] may also be found in the resulting framework.^[8,15] However, in the present case, it is the conjugate base of added acetic acid, which has served as anionic linker. As far as it is known, compound **1** provides the first reported

example of a 3D paddle-wheel-based MOF in which an anion acts as a bridging ligand to extend 2D carboxylate layers into a 3D structure.

Thermogravimetric Analysis (TGA), Flowing SC-CO₂ Activation, and N₂ Adsorption Isotherm

The thermogravimetric analysis (TGA) performed on a sample of as-synthesized **1** showed a continuous mass loss of 45% in the temperature range 25–270 °C (Figure 5). This mass loss can be assigned to the removal of three DEF molecules and one diethylammonium acetate per formula unit (calcd. 43.8%). The remaining residue decomposes between 320 °C and 440 °C and, according to PXRD, leads to the formation of ZnO after being heated above 450 °C. The total mass loss of the sample is about 82%, in accordance with the calculated value of 83.6% for (H₂NEt₂)[Zn₂(AcO)(NDC)₂]+3DEF.

The lack of a well-defined plateau at ca. 30% mass loss, which would have been consistent with the removal of three DEF molecules and the occurrence of a guest-free 3D framework, actually suggests that hydrogen bonded DEF molecules constitute an important element in ensuring the stability of the acetate-based 3D framework of **1**. One method to assess the crystallographic aperture of **1** is to measure the BET (Brunauer-Emmett-Teller) surface area from a desolvated sample.

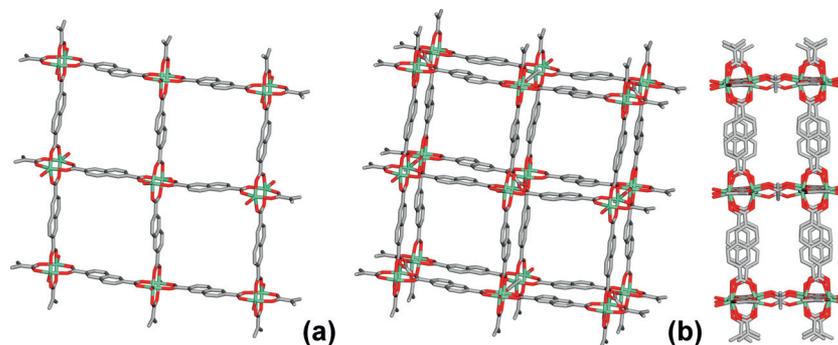


Figure 3. Crystal structure of **1** involving 2D paddle-wheel based Zn-NDC layers (a), interconnected by bridging acetates into a 3D framework (b) (hydrogen atoms and diethyl ammonium cations are omitted. Color code: Zn: green; N: blue; O: red; C: gray).

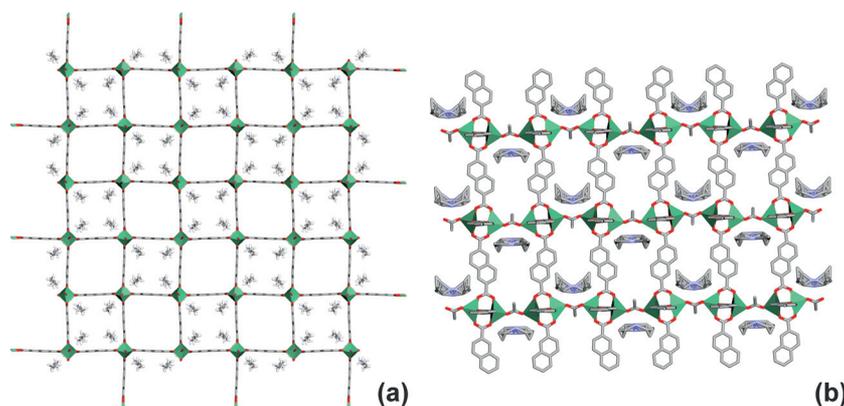


Figure 4. (a) View of the anionic framework of **1** with channels alternatively occupied and unoccupied by the diethylammonium counter-cations. (b) Inter-layer acetate linkages involved in framework **1** with the disordered diethylammonium counter-cations. Hydrogen atoms are omitted except for the diethylammonium cations in view (a) (color code: Zn: green; C: gray; H: white; N: blue; O: red).

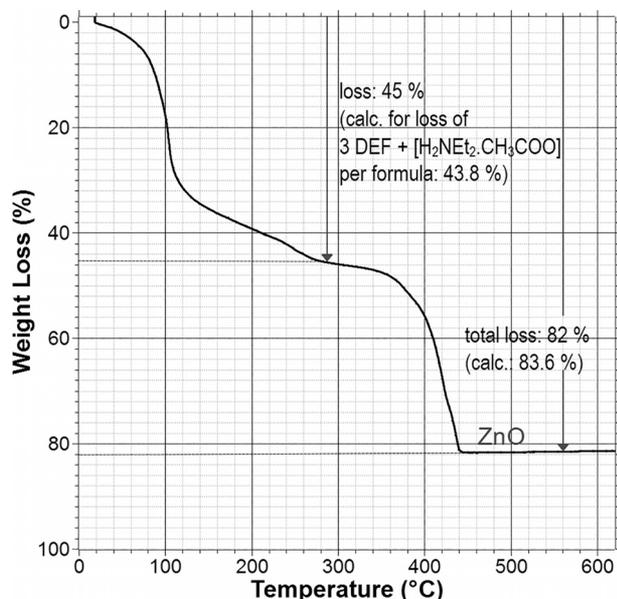


Figure 5. TGA curve of as-synthesized **1**, revealing a 45 % weight loss between 18 and 272 °C corresponding to the loss of 3DEF and one diethylammonium acetate (calcd. 43.8%), and a total weight loss of about 82 % (calcd. 83.6%) leading to the formation of ZnO in accordance with the molecular formula $(\text{H}_2\text{NEt}_2)[\text{Zn}_2(\text{AcO})(\text{NDC})_2]\cdot 3\text{DEF}$.

For activating **1**, it was therefore opted for the recently reported flowing supercritical CO_2 (SC- CO_2) procedure^[16] which is often the only possibility to desolvate fragile frameworks without network transformation.^[17] However, as suggested by elemental analysis (refer to Experimental Section) and TGA, activation of **1** by flowing SC- CO_2 affords a deacetylated sample, referred to as **1-SC**, which exhibits a negligible BET surface area of $54 \text{ m}^2\text{g}^{-1}$ (Figure 6), revealing a structural collapse of the framework during DEF removal.

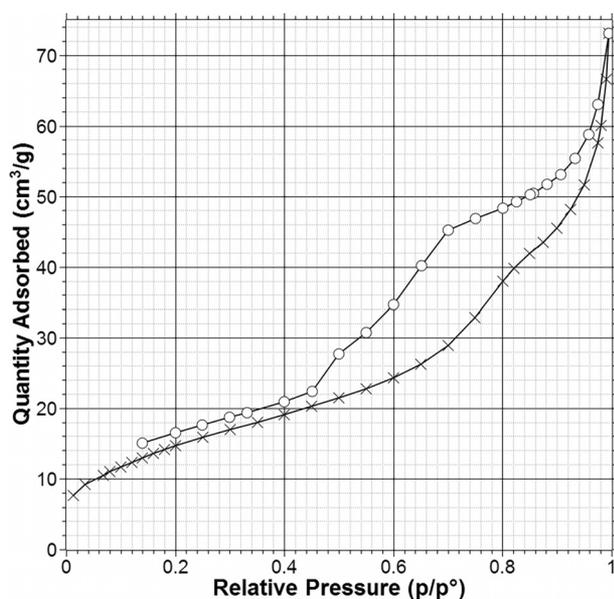


Figure 6. Nitrogen sorption isotherm of **1-SC** at 77 K after activation by flowing SC- CO_2 [adsorption (x) and desorption (o)].

Conclusions

A zinc-2,6-naphthalenedicarboxylate metal-organic framework (**1**) was solvothermally synthesized. Although **1** is based on one of the most common SBUs – the square $\text{Zn}_2(\text{O}_2\text{CR})_4$ paddle-wheel unit – it represents the first example of a 3D paddle-wheel MOF, in which the zinc-dicarboxylate sheets are connected into a three-dimensional structure through an anionic bridging agent (i.e., the acetate ion). The resulting anionic framework of **1** exhibits large square channels containing DEF molecules and charge-balancing diethylammonium cations. Attempts to remove DEF solvent molecules without damaging the three-dimensional framework of **1** were unsuccessful, even when the relatively mild conditions of the flowing supercritical CO_2 procedure were used. It has been reported that zinc-paddle-wheel based MOFs frequently undergo partial or complete collapse due to axial ligand exchange or distortion of the dimeric zinc SBU under dry conditions.^[18] Such chemical sensitivity is likely to be even more pronounced for anionic paddle-wheel frameworks like **1** as extra-framework counter-cations also play a crucial role in structural integrity.

Experimental Section

General: All reagents and solvents were purchased from commercial sources (Sigma Aldrich or Alfa Aesar) and were used without further purification. Synthesis of **1** was carried out in 2–5 mL glass vials. Elemental analyses were measured with a EuroVector EuroEA. Thermogravimetric analysis was performed in flowing air (heating rate $3 \text{ K}\cdot\text{min}^{-1}$) with a Setaram TAG-16 analyzer. The samples were held in platinum pans. Micromeritics ASAP 2020 (USA) was used to measure the surface area of the sample using nitrogen adsorption/desorption isotherms. A known amount of sample (49.1 mg) was loaded into the BET sample tube and degassed under vacuum (10^{-5} Torr) at room temperature for 1 h. The BET specific surface area was calculated from the adsorption isotherm. Single-crystal X-ray diffraction were performed with a Bruker-AXS kappa APEX II Quazar diffractometer with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 153(2) K. The powder X-ray diffraction patterns were collected with an XPert Pro (Theta-Theta mode) Panalytical powder diffractometer with λ ($\text{Cu-K}\alpha_1$, $-\text{K}\alpha_1$) = 1.54059, 1.54439 Å.

Synthesis of $(\text{H}_2\text{NEt}_2)[\text{Zn}_2(\text{AcO})(\text{NDC})_2](\text{DEF})_n$ (1**):** 2,6-Naphthalenedicarboxylic acid (H_2NDC , 139.7 mg, 0.64 mmol, 1.0 equiv.) and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (680.0 mg, 2.24 mmol, 3.5 equiv.) were dissolved in DEF (16 mL) containing acetic acid (366 μL , 10.0 equiv.) and sealed in a glass vial. The vial was heated to 130 °C for 5 h. After cooling to room temperature, the reaction mixture was allowed to stand 7–10 d until colorless needle-like crystals formed. The crystals were collected by filtration, washed with DEF several times and kept under fresh DEF until required for characterization. Yield: 200 mg (63 % based on H_2BDC and $n = 3$). A number of attempts to obtain satisfactory elemental analysis have proved to be unsuccessful, possibly because of facile solvent loss and concomitant hydration. However, the identity of the as synthesized bulk material was confirmed by comparing the X-ray powder diffraction pattern with that simulated from the crystal structure (Figure 1).

Flowing SC- CO_2 Activation: As synthesized DEF-solvated crystals of **1** (88.7 mg) were transferred into a 2.1 mm i.d \times 50 mm stainless steel column. The column was connected to a supercritical CO_2 system

(SFC-PICLAB Analytic apparatus equipped with HPLC K-501 Knauer pumps) with a back pressure regulator set at 100 bar. The CO₂ was pumped at a flow rate of 2 mL·min⁻¹ and the column was heated at 35 °C through a column heater. Detection was achieved with a UV/Vis monitor (Smartline UV 2600 Knauer detector) set at 210 nm. Under such conditions, a flowing time of 3 h was required to get zero detection. Thus, after flowing of CO₂ for 3 h, the flow was stopped and supercritical CO₂ in the column was gradually released to atmosphere. The activated sample (**1-SC**, 59.4 mg) in the column was transferred to a sorption cell in a N₂ glove box and the surface area was measured. Elemental analysis for **1-SC** (C 49.76, H 3.96, N 2.07%) is in agreement with the chemical formula Zn₂(NDC)₂(DEF)(H₂O)₂ (C₂₉H₂₇NO₁₁Zn₂; calcd. C 50.02, H 3.91, N 2.01%).

Structure Determination and Refinement: Intensity data for compound **1** were collected at a temperature of 153(2) K using Mo-K_α radiation (wavelength = 0.71073 Å) with a Bruker-AXS APEX II Quazar diffractometer using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics. Phi- and omega scans were used. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied (SAINT; Bruker AXS Inc.: Madison, Wisconsin, 2000; SADABS, Program for data correction, Bruker-AXS). The structure was solved by direct methods, using SHELXTL Software Package, and refined using the least-squares method on F².^[19] All non-H atoms were treated anisotropically. The hydrogen atoms were fixed geometrically and treated as a riding model. The diethylammonium cation was found disordered over two positions. The disorder was modeled using some restraints: SAME, SADI, SIMU, DELU and ISOR. Attempts were made to model the disorder of the solvent (presumably *N,N*-diethylformamide) but were unsuccessful. Therefore, the SQUEEZE function of PLATON^[20] was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement. Crystallographic data and structure refinement results are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1403903 for compound **1** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

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Table 1. Crystal data and structure refinement for **1**.

	1
Empirical formula	C ₃₀ H ₂₇ NO ₁₀ Zn ₂
Formula weight	692.26
Temperature /K	153(2)
Wavelength /Å	0.71073
Crystal system	tetragonal
Space group	<i>P4(2)/mbc</i>
Unit cell dimensions	
<i>a</i> /Å	26.0852(10)
<i>b</i> /Å	26.0852(10)
<i>c</i> /Å	17.6308(6)
Volume /Å ³	11996.7(10)
<i>Z</i>	8
Density (calculated) /Mg·m ⁻³	0.767
Absorption coefficient /mm ⁻¹	0.829
<i>F</i> (000)	2832
Crystal size /mm ³	0.500 × 0.300 × 0.200
Theta range for data collection /°	1.104 to 28.282
Index ranges	−34 ≤ <i>h</i> ≤ 34 −34 ≤ <i>k</i> ≤ 34 −23 ≤ <i>l</i> ≤ 21
Reflections collected	206677
Independent reflections	7659 [<i>R</i> (int) = 0.0715]
Completeness to θ = 25.242°	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6738
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	7659 / 199 / 267
Goodness-of-fit on <i>F</i> ²	1.075
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0457, <i>wR</i> ₂ = 0.1190
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0739, <i>wR</i> ₂ = 0.1416
Largest diff. peak and hole /e·Å ⁻³	0.695 and −0.537

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