Keywords: boron · N ligands · porphyrinoids

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[3] Crystal structure analysis of $\mathbf{4}\cdot 2\,CHCl_3\cdot C_6H_6$: $C_{44}H_{24}B_4Cl_{10}N_4O_2\cdot 2\,CHCl_3\cdot C_6H_6$: $M_r = 1355.26$, triclinic, space group $P\bar{1}$, $T = 193$ K, $a = 10.238(12)$, $b = 10.272(3)$, $c = 27.865(7)$ Å, $\alpha = 97.33(2)$, $\beta = 97.64(5)$, $\gamma = 96.18(5)^\circ$, $V = 2857(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.575\ g\,cm^{-3}$, $F(000) = 1360$. Suitable crystals were grown from a solution in $CHCl_3$ saturated with $BCl_3\cdot MeCN$. The crystals were small ($0.20 \times 0.12 \times 0.12$ mm), of poor quality, and only weakly diffracting, which limited the data quality and hence the final precision. Enraf-Nonius CAD-4 diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Total of 9008 reflections to $2\theta = 50^\circ$. Semi-empirical absorption correction (Ψ scans, $\mu = 0.81\ mm^{-1}$, $A_{min}/A_{max} = 0.907/0.922$). The structure was solved by direct methods and refined by full-matrix least squares on F^2 with all data. The unit cell contains two independent half-molecules, each related through a center of symmetry, as well as one benzene and two chloroform molecules per porphyrin molecule. All atoms were allowed to refine anisotropically, and hydrogen atoms were included with a riding model. Refinement converged to $R = 0.0937$ for the 4249 observed data ($I > 2\sigma I$) and $wR2 = 0.2924$ for all data. Goodness of fit on $F^2 = 0.973$. Programs used: SHELXS (structure solution) and SHELXL (structure refinement). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100798 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Topochemical Conversion of a Hydrogen-Bonded Three-Dimensional Network into a Covalently Bonded Framework[**]

John D. Ranford,* Jagadese J. Vittal,* and Daqing Wu

The design and construction of supramolecular, three-dimensional networks has been an area of increasing interest over recent years with respect to engineering crystal packing at will.[1] Strategies for crystal engineering include the use of various intermolecular forces, from weak van der Waals forces, hydrogen and covalent bonding,[2, 3] to ionic interactions.[4] Most of the reported three-dimensional architectures are formed as a result of self-assembly from solution.[5] An exciting, yet little explored area of supramolecular chemistry, is the reversible interconversion between monomers and oligomers initiated by the input of external information (e.g. protons, electrons, photons). Such materials may have functional use due to their switching ability and the possibility to sequester and release guest molecules. Recently a proton-dependent monomer–oligomer interconversion in solution was reported.[6] Here we report the topochemical thermal conversion of a novel, three-dimensional network held together by strong hydrogen bonding into a covalent, supramolecular framework by dehydration of coordinated water. This unexpected transformation of hydrogen-bonded to covalent network appears to be assisted by strong NH···O hydrogen bonds and irreversible.

$[\{Zn(sala)(H_2O)_2\}_2]\cdot 2\,H_2O$ (**1**) was prepared by the reaction of $Zn(ClO_4)_2\cdot 6\,H_2O$ with $Li_2(sala)$ in aqueous solution and characterized by single-crystal X-ray diffraction techniques[7] ($H_2(sala)$ = *N*-(2-hydroxybenzyl)-L-alanine). Figure 1 shows the structure of the basic dimeric building block,

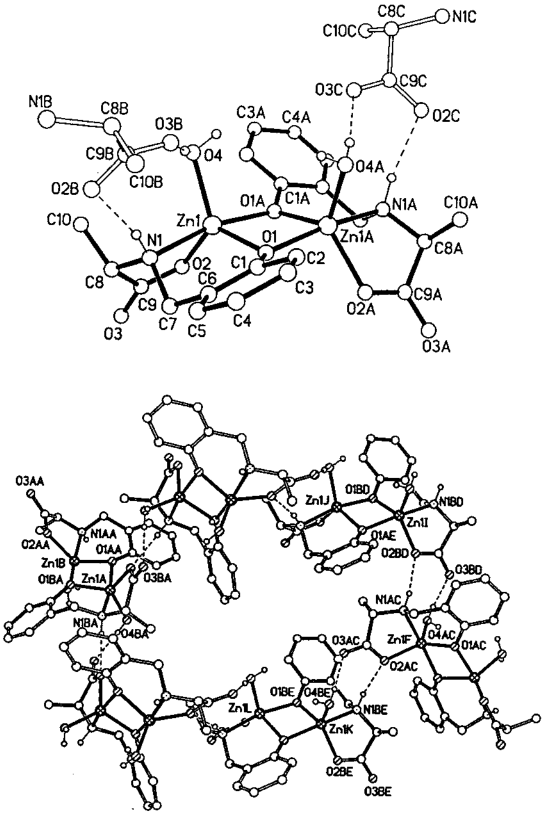

Figure 1. Top: Structure of the binuclear complex **1**. Hydrogen bonds are drawn with dotted lines. The hydrogen atoms attached to carbon atoms are omitted for clarity. Selected fragments of neighboring molecules involved in hydrogen bonding are shown with open bonds. Selected bond distances [Å] and angles [°]: Zn1···Zn1A 3.092(1), Zn1–O1 2.009(2), Zn1–O1A 2.040(2), Zn1–O2 2.027(2), Zn1–O4 2.030(2), Zn1–N1 2.140(2), C9–O2 1.270(4), C9–O3 1.246(4); Zn1-O1-Zn1A 99.58(7), O1-Zn1-N1 93.00(8), O1-Zn1-O1A 79.56(8), O2-C9-O3 124.1(3). Bottom: The hydrogen bonds link the dimers together to form hexagonal rings.

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$[\{Zn(sala)(H_2O)_2\}_2]$, along with the coordination around the Zn^{II} centers and the hydrogen-bonding network. The zinc center has distorted square pyramidal geometry with the base comprised of the tridentate, dianionic sala ligand and the bridging phenolate moiety. Water completes the coordination sphere in the apical site. The crystallographically imposed twofold symmetry results in the two water molecules being on the same side of the dimeric unit. The dimer has two sets of NH and OH_2 hydrogen donors and two carboxylate anions as acceptors. The presence of complementary molecular functionalities leads to efficient hydrogen bonding[8] between the neutral dimeric complexes (Figure 1, bottom). Six dimers link to give a hexagonal ring containing ten zinc centers. The carboxylate oxygen atoms (O3) that are not involved in bonding in the ring act as acceptors for hydrogen bonds to bound water molecules in other rings, thus linking together the ten-membered hexagonal rings. The result is a honeycombed, open-framework coordination polymer (Figure 2).

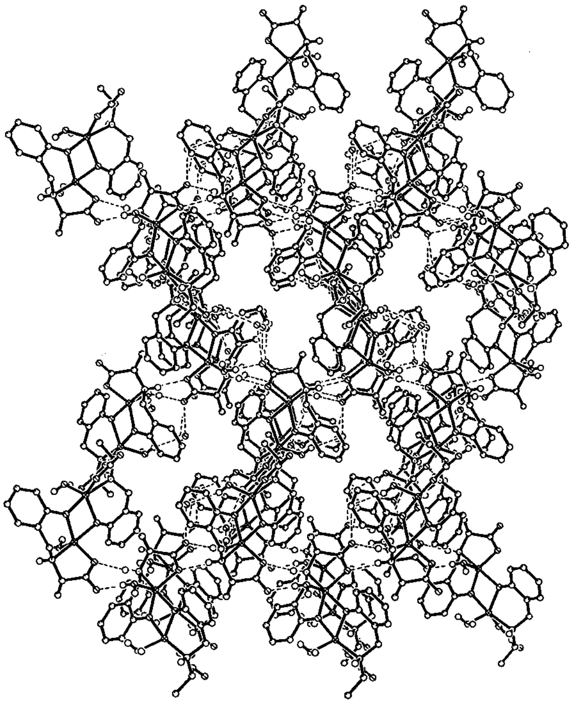


Figure 2. View of **1** along the crystallographic axis *b* illustrating the channels of the open-framework coordination polymer.

The hydrogen-bonded network in **1** provides favorable conditions for the topochemical reaction to take place. The geometric proximity between the Zn centers and the carboxylate oxygen atoms from adjacent molecules in **1** (e.g. Zn1···O3C 3.736(2) Å) is maintained by OH···O hydrogen bonding. Thermal dehydration can remove ligated and nonbonded water, which can then escape through the channels without disrupting the solid-state structure.[9] Minimal atom movements and conformational changes are anticipated during dehydration.

On heating, all water molecules are lost from **1**.[10, 11] The X-ray structure determination[12] of the anhydrous compound, $[\{Zn(sala)\}_n]$ (**2**), reveals a number of unique features (Figure 3). The structure of this solid-state dehydration product[13] **2** bears a close relationship to that of the reactant **1**; they have the same crystal and point-group symmetry. Owing to the chiral ligand, the space group is also chiral. In **1** and **2** the channels are helical in nature and therefore orient in the same direction. The intermolecular interactions stabilizing the structure have changed from hydrogen bonding only in **1** to both covalent and hydrogen bonding in **2**, as shown in Figure 3 and Scheme 1. It is interesting to note that the NH···O hydrogen bonding[14] is preserved in **2**. From the proximity of the atoms Zn1 and O3 in **1** and the presence of NH···O hydrogen bonding in both **1** and **2**, it appears that the Zn–O(carboxylate) bond formation is aided by the presence of both hydrogen-donor N–H groups and hydrogen acceptors in the binuclear complex. This appears to be the first example of topochemical conversion of a hydrogen-bonded into a

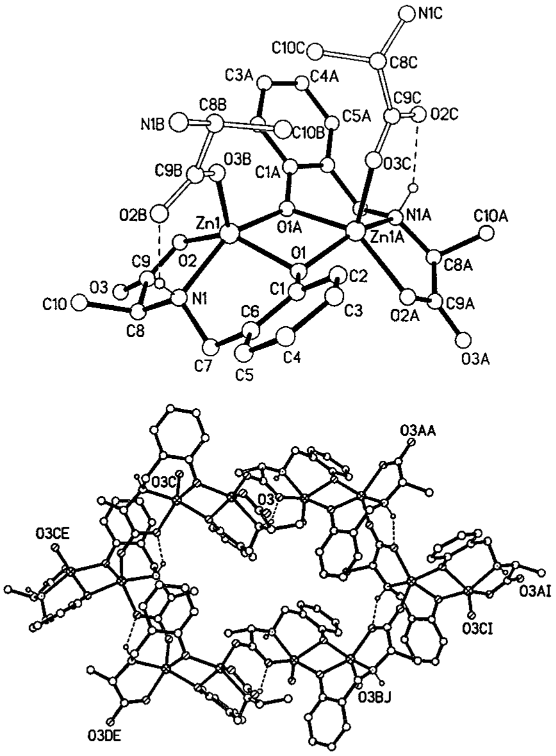
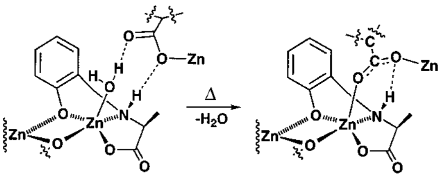


Figure 3. Top: Structure of the dimeric unit of **2**. Hydrogen bonds are drawn with dotted lines. Selected bond distances [Å] and angles [°]: Zn1···Zn1A 3.152(1), Zn1–O1 2.072(1), Zn1–O1A 1.999(1), Zn1–O2 2.073(1), Zn1–O3A 2.017(1), Zn1–N1 2.108(1), C9–O2 1.258(2), C9–O3 1.260(2); Zn1-O1-Zn1A 101.48(4), O1-Zn1-N1 90.39(4), O1-Zn1-O1A 77.19(4), O2-C9-O3 125.1(1). Bottom: A segment of the three-dimensional network of **2**. The close resemblance to **1** which results from the topochemical dehydration and formation of the covalent Zn1–O2 bond can be seen.



Scheme 1. Coordination environments and hydrogen bonding in the hydrated **1** and dehydrated **2**, illustrating the transformation from hydrogen bonding to covalent bonding.

covalent-bonded supramolecular network. Attempts to rehydrate **2** to give **1** have been unsuccessful; therefore, dehydration appears to be irreversible.

Experimental Section

The synthesis of H_2(sala) was adapted from reference [15]: Salicylaldehyde (134 mg, 1.10 mmol) in ethanol (10 mL) was added to a solution of L-alanine (89 mg, 1.00 mmol) and KOH (56 mg, 1.00 mmol) in water (10 mL). The yellow solution was stirred for 30 min at room temperature prior to cooling in an ice bath. The pH was adjusted to 6–7 with acetic acid, and then $NaBH_4$ (46 mg, 1.20 mmol) was added. After 15 min the yellow color had discharged and the solution was acidified with acetic acid to pH 5.0 and left for one hour. The product was filtered off, washed with ethanol and diethyl ether, dried in vacuo, and recrystallized from water/ethanol (1/1). Yield: 109 mg (56%), m.p. 241–242 °C, $[\alpha]^{30}_{\mathrm{L}} = -22.2$ ($c = 0.5$ in water).

1: H_2(sala) (195 mg, 1.00 mmol) was added to a solution containing LiOH (48 mg, 2.00 mmol) and $CH_3CO_2Na \cdot 3\,H_2O$ (136 mg, 1.00 mmol) in water (20 mL). A solution of $Zn(ClO_4)_2 \cdot 6\,H_2O$ (372 mg, 1.00 mmol) in water (10 mL) was gradually added to the above stirred solution. The mixture was stirred for 30 min, filtered, and kept at room temperature for several days to yield distorted, octahedral-shaped crystals. The crystals were separated by decantation and dried in air. Yield: 191 mg (65%). C,H,N analysis: calcd for $C_{10}H_{15}NO_5Zn$: C 40.7, H 5.1, N 4.7; found: C 40.4, H 5.1, N 4.5; IR (KBr): $\tilde{\nu} = 1588$ (s, $\nu_{as}(CO_2)$), 1413 (s, $\nu_s(CO_2)$), 1282 cm^{-1} (s, ν(C-O)$_{carb}$).

2: A solution of H_2(sala) (195 mg, 1.00 mmol) and LiOH (24 mg, 1.00 mmol) in water (10 mL) was added to a solution of $Zn(ClO_4)_2 \cdot 6\,H_2O$ (372 mg, 1.00 mmol) in water (10 mL). The solution was stirred for 30 min and left at room temperature to evaporate. Large, distorted diamond-shaped, colorless crystals were separated by decantation and dried in air. Yield: 176 mg (68%). C,H,N analysis: calcd for $C_{10}H_{11}NO_3Zn$: C 45.6, H 4.4, N 5.3; found: C 45.4, H 4.7, N 5.1; IR (KBr): $\tilde{\nu} = 1598$ (s, $\nu_{as}(CO_2)$); 1404 (s, $\nu_s(CO_2)$); 1284 cm^{-1} (s, ν(C-O)$_{carb}$).

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[7] Crystal structure determination of **1**:[16] Tetragonal, space group $P4_32_12$, $a = 10.7799(1)$, $c = 23.0372(1)$ Å, $V = 2677.07(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.462\ g\,cm^{-3}$. All H atoms were located successfully. Positional and isotropic thermal parameters were refined for the H atoms in the coordinated water molecules, and riding models were used for the rest. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1 = 0.0333$, $wR_2 = 0.0609$, and GOF = 1.090 for 2808 reflections with $F_o > 4\sigma(F_o)$ and 182 parameters, and $R_1 = 0.0504$ and $wR_2 = 0.0662$ for all 3385 data. The Flack parameter x was refined to 0.003(15).

[8] Close intermolecular hydrogen-bonding distances [Å] and angles [°]: O2 ··· H1 2.050, O3 ··· H4B 1.857, O2 ··· N1 2.950, O3 ··· O4 2.645; O2-H1-N1 169.6, O3-H4B-O4 174.0.

[9] The channels are oval with approximate dimensions 7 × 10 Å (non-hydrogen contacts). However, the alternating, stacked arrangement means that the effective pore size is bigger than this. The channels are occupied by (disordered) water molecules and held together by hydrogen bonds. Selected hydrogen-bonded distances [Å]: O3 ··· O5 2.771, O3 ··· O5A 2.781, O3 ··· O5B 2.556.

[10] Thermogravimetric analysis of **1** indicated a weight loss of 11.2% in the temperature range 50–120 °C, corresponding to the loss of two molecules of water (expected weight loss 12.2%) and the formation of the anhydrous compound **2**. The X-ray powder pattern of this anhydrous material was the same as that of **2**. Both **1** and **2** show the same decomposition pattern, which starts at about 340 °C.

[11] The structures of the bulk materials for **1** and **2** were confirmed by matching their X-ray powder patterns with those generated from the corresponding single crystals. Compound **2** was also prepared independently. The crystal structure was carried out on the single crystal grown from aqueous solution.

[12] Crystal structure determination of **2**:[16] Tetragonal, space group $P4_32_12$, $a = 8.997(1)$, $c = 24.571(4)$ Å, $V = 1988.8(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.727\ g\,cm^{-3}$. All H atoms were located successfully and refined with riding models. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1 = 0.0152$, $wR_2 = 0.0422$, and GOF = 1.031 for 2525 reflections with $F_o > 4\sigma(F_o)$ and 138 parameters, and $R_1 = 0.0158$ and $wR_2 = 0.0425$ for all 2571 data. The Flack parameter x was refined to $-0.004(8)$.

[13] The single crystal of **1** became opaque and brittle on heating at 90 °C for two hours.

[14] Distances [Å] and angles [°] of the hydrogen bonds: O2 ··· H1 2.161, O2 ··· N1 2.944; N1-H1-O2 144.

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[16] General crystallographic details: Data were collected on a Siemens SMART CCD system with graphite-monochromated $Mo_{K\alpha}$ radiation and a sealed tube (2.4 kW) at 23 °C. Absorption corrections were made with the program SADABS (G. M. Sheldrick, Göttingen, 1996), and the crystallographic software package SHELXTL (SHELXTL Reference Manual, Version 5.03, Wisconsin, 1996) was used for all calculations. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100837. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).