Inorg. Chem. **2005**, *44*, 5200–5202

Inorganic Chemistry
Communication

A Nearly Planar Water Sheet Sandwiched between Strontium–Imidazolium Carboxylate Coordination Polymers

Zhaofu Fei, Tilmann J. Geldbach, Dongbin Zhao, Rosario Scopelliti, and Paul J. Dyson*

Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Received March 22, 2005

The crystal structure of a strontium–imidazolium polymeric material obtained from the reaction of zwitterionic 1,3-bis(carboxymethyl)-imidazolium with $SrCO_3$ (2:1) in water is reported. The compound crystallized in the orthorhombic space group *Pcc*2 with $a = 14.545(3)$ Å, $b = 8.514(5)$ Å, $c = 8.5619(14)$ Å, $V = 1060.2(6)$ Å^3, and $Z = 2$. The macromolecular structure is constructed from 8-coordinate strontium, which binds to six different imidazolium carboxylate molecules. The two-dimensional polymer is separated by water sheets in which the water molecules form near-planar hexagons.

Water has generated more interest than any other small molecule because of its fundamental importance in many biological and chemical processes.[1] Despite extensive studies, water remains a poorly understood liquid, although recent investigations on the properties of water clusters,[2] water oligomers in supramolecular crystals,[3] and low-dimensional water polymers in supramolecular solids[4] have provided new impetus. Although the latter play a crucial role in stabilizing the native conformation of biopolymers, such polymeric water networks are rare in synthetic crystal hosts.

Of the numerous different configurations of water oligomers, the hexamer is of particular interest, as it is considered the smallest unit that can exhibit the properties of bulk water.[2b] Cyclic water hexamers may, for example, be isolated in liquid helium and analyzed by spectroscopy.[2a] Water oligomers may also be stabilized in molecular matrixes, including planar hexamers found in the structure of bimesityl-3,3′-dicarboxylic acid,[5] extended water tapes in an organic host,[6] and hexameric clusters with a puckered-boat conformation in a copper−carboxylic acid framework.[7] Apart from inclusion complexes containing water clusters and chains, crystals with two-dimensional water layers sandwiched between organic/inorganic frameworks are also known.[8] Water layers sandwiched between nickel(II) chelate complexes were even found to undergo structural changes as a function of the temperature, giving rise to condensed 8- and 12-membered rings, as demonstrated by neutron diffraction.[9]

In general, the incorporation of water clusters or networks into polymeric architectures is accomplished using synthons that are rich in hydrogen bond donor/acceptor groups,[4,10] with inter- and intramolecular hydrogen bonding and other noncovalent interactions being the main driving forces for the assembly of such systems. The imidazolium cation contains three acidic protons that can be harnessed in hydrogen-bonding networks,[11] and they have already been used to generate hydrogen-bond-driven polymeric systems.[4b,12] Herein, we report a nearly planar hydrogen-bonding stabilized water sheet interspersing a two-dimensional coordination polymer,

---

* Author to whom correspondence should be addressed. E-mail: paul.dyson@epfl.ch.

(1) (a) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808. (b) Ohmine, I.; Saito, S. *Acc. Chem. Res.* **1999**, *32*, 741.
(2) (a) Nauta, K.; Miller, R. E. *Science* **2000**, *287*, 293. (b) Gregory, J. K.; Clary, D. C.; Liu, K.; Brown, M. G.; Saykally, R. J. *Science* **1997**, *275*, 814. (c) Liu, K.; Brown, M. G.; Carter, C.; Saykally, R. J.; Gregory, J. K.; Clary, D. C. *Nature* **1996**, *381*, 501. (d) Liu, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929. (e) Ugalde, J. M.; Alkorta, I.; Elguero, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 717. (f) Ma. B.-Q.; Sun, H.-L.; Gao, S. *Chem. Commun.* **2004**, 2220.
(3) (a) Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 7192. (b) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Chem. Commun.* **2000**, 859. (c) Blanton, W. B.; Gordon-Wylie, S. W.; Clark, G. R.; Jordan, K. D.; Wood, J. T.; Geiser, U.; Collins, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3551. (d) Gruenloh, C. J.; Carney, J. R.; Arrington, C. A.; Zwier, T. S.; Fredericks, S. Y.; Jordan, K. D. *Science* **1997**, *276*, 1678.
(4) (a) Pal, S.; Sankaran, N. B.; Samanta, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1741. (b) Cheruzel, L. E.; Pometun, M. S.; Cecil, M. R.; Mashuta, M. S.; Wittebort, R. J.; Buchanan, R. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5452. (c) Sreenivasulu, B.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5769.
(5) Narasimha Moorthy, J.; Natarajan, R.; Venugopalan, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 3417.
(6) Custelcean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3094.
(7) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 5180.
(8) (a) Nightingale, D. J.; Cronin, L.; Clark, J. H. *Acta Crystallogr. C* **1997**, *53*, 789. (b) Yamazaki, M.; Sasaki, C.; Kakiuchi, H.; Osano, Y. T.; Suga, H. *Thermochim. Acta* **2002**, *387*, 39.
(9) Janiak, C.; Scharmann, T. G.; Mason, S. A. *J. Am. Chem. Soc.* **2002**, *124*, 14010.
(10) See, for example, (a) Zhao, B.; Cheng, P.; Chen, X.; Cheng, C.; Shi, W.; Liao, D.; Yan, S.; Jiang, Z. *J. Am. Chem. Soc.* **2004**, *126*, 3012. (b) Dong, Y. B.; Zhao, X.; Tang, B.; Wang, H. Y.; Huang, R. Q.; Smith, M. D.; zur Loye, H.-C. *Chem. Commun.* **2004**, 220. (c) Runde, W. Bean, A. C.; Scott, B. L. *Chem. Commun.* **2003**, 1848.
(11) Katsyuba, S. A.; Dyson. P. J.; Vandyukova, E. E.; Chernova, A. V.; Vidis, A. *Helv. Chim. Acta* **2004**, *87*, 2556.
(12) Fei, Z.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *Chem. Eur. J.* **2004**, *10*, 4886.

10.1021/ic0504238 CCC: $30.25

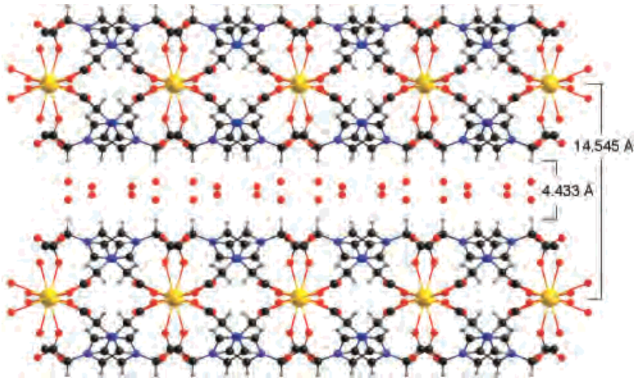

Figure 1. View along the *c* axis of **1**; hydrogen atoms at the water molecules have been omitted for clarity. (Sr is in yellow).

Table 1. Crystallographic Data for $(C_7H_7N_2O_4)_2Sr{\cdot}4H_2O$

chemical formula	$C_{14}H_{22}N_4O_{12}Sr$
formula weight	525.98
space group	*Pcc*2
a	14.545(3) Å
b	8.514(5) Å
c	8.5619(14) Å
T	140(2) K
λ	0.71070 Å
V	1060.2(6) Å^3
Z	2
D_{calcd}	1.648 Mg/m^3
μ	2.611 mm^{-1}
final *R* indeces [$I > 2\sigma(I)$]	R1 = 0.0327, wR2 = 0.0792
R indeces (all data)	R1 = 0.0365, wR2 = 0.0809

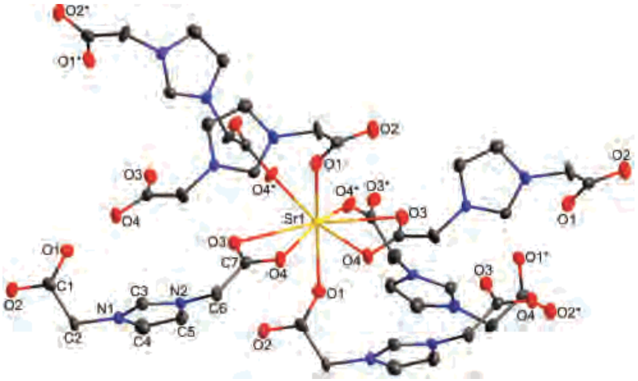

Figure 2. Coordination around the strontium atom; ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sr1−O1, 2.482(3); Sr1−O3, 2.810(3); Sr1−O4, 2.641(4); Sr1−O4*, 2.515(4); C1−O1, 1.245(5); C1−O2, 1.255(5); C7−O3, 1.240(5); C7−O4, 1.265(5); N1−C3, 1.324(5); N1−C4, 1.366(6); N2−C3, 1.321(4); N2−C5, 1.349(6); C4−C5, 1.364(6); C1−O1−Sr1, 145.4(3); O1−C1−O2, 126.3(4); O3−C7−O4, 124.8(4).

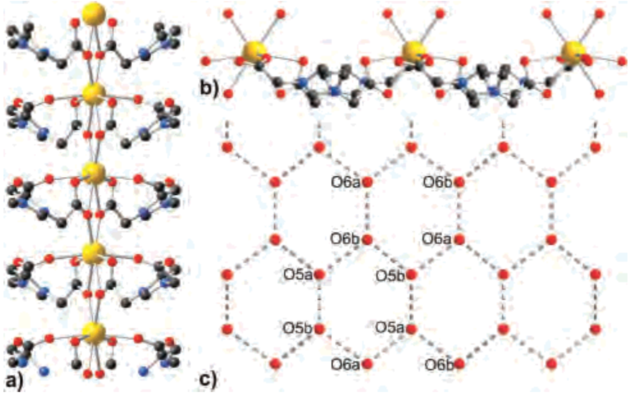

Figure 3. (a) Coordination in the polymer along the *b* axis. (b) Coordination in the polymer along the *a* axis; View of the water sheet along the *bc* plane with selected bond lengths (Å) and angles (°): O5a−O5b, 2.779(4); O6a−O6b, 2.824(4); O5a−O6a, 2.788(5); O5a−O6b, 2.759(5); O5b−O6a, 2.759(6); O5b−O6b, 2.789(6); O5−O6−O5, 102.3(2); O6−O5−O6, 106.7(2).

which is isolated from the reaction between a carboxylic acid-functionalized imidazolium salt and strontium carbonate.

Treatment of the zwitterion 1,3-bis(carboxymethyl)imidazolium with 0.5 equiv of $SrCO_3$ in water at room temperature yields a clear solution from which colorless prismatic crystals of $(C_7H_7N_2O_4)_2Sr{\cdot}4H_2O$, **1**, form as the concentration of the solution increases due to slow evaporation of the solvent. Analysis of **1** by single crystal X-ray diffraction methods (see Table 1) reveals the polymeric structure shown in Figure 1, in which a two-dimensional water layer is segregated by layers composed of the strontium−imidazolium 2D network.

In **1**, each strontium(II) cation is surrounded by eight oxygen atoms, stemming from six different imidazolium molecules, which form a distorted hexagonal bipyramid geometry (see Figure 2). Two carboxylate groups act as chelate ligands with O−Sr bond distances of O3−Sr1 = 2.810(3) Å and O4−Sr1 = 2.641(4) Å, and the remaining four bind in a unidentate mode [O1−Sr1 = 2.482(3) Å]. Oxygen atom O4 further bridges to another metal center [O4−Sr1 = 2.515(4) Å], resulting in an oxygen-bridged strontium chain [Sr···Sr = 4.2810(7) Å].

These chains are interwoven by chain-bridging imidazolium dicarboxylates, the distance between the strontium ions in different rows being 8.514(5) Å (Figure 3b). Eight-coordinate strontium which is bound to six carboxylate ligands has been previously observed in crystals of anhydrous $Sr[C_2(COO)_2]$ with O−Sr distances ranging between 2.507(2) and 2.751(2) Å[13] and in $[Sr_3(OCSOEt)_6(EtOH)_8]$, where the distance of the central strontium atom to the eight surrounding oxygen atoms lies between 2.521(5) and 2.764(6) Å.[14]

Oxygen atom O2 is not involved in bonding to the metal cation but interacts with the water layer via hydrogen bonding [O2···O6 = 2.689(2) Å]. Additionally, much longer hydrogen bonds stem from C2 [H2B···O6 = 2.662 Å] and from C4 [H4A···O5 = 2.417 Å].

The water layer is almost planar with a hexagonal arrangement of the water molecules in the *bc* plane. There are two independent, edge-shared hexamers, of which one has an envelope, the other a twisted boat conformation. The O···O distances within the hexamer range from 2.759(5) to 2.824(4) Å, which is slightly shorter than the distance found in liquid water, 2.85 Å.[15] The deviation of the oxygen atoms from the mean plane of water hexamers is 0.25 and 0.43 Å, respectively. The size of the water-filled gap between the polymer layers is approximately 4.5 Å, with

---

(13) Hohn, F.; Pantenburg, I.; Ruschewitz, U. *Chem. Eur. J.* **2002**, *8*, 4536.

(14) Bezougli, I. K.; Bashall, A.; McPartlin, M.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1997**, 287.

(15) Narten, A. H.; Thiessen, W. E.; Blum, L. *Science* **1982**, *217*, 1033.

the shortest distance spanning from H4···H4 (4.43 Å). Of the acidic imidazolium protons, namely H3, but also H4 and H5, only H4 is engaged in hydrogen bonding to water molecules. The other two protons form hydrogen bonds to nearby carboxylic acid oxygen atoms. It is possibly the presence of relatively weak hydrogen-bonding protons on the imidazolium, which allow the water molecules to form hydrogen bonds with each other, thereby generating the water sheet rather than forming more-extensive hydrogen bonding to the organic part of the structure.

Two-dimensional, hexagonal water layers have been observed previously.[16] The overall structure further bears a close resemblance to, for example, that observed in montmorillonite clays where water molecules are easily absorbed between the layers, leading to a swelling of the mineral.[17] Yet, it is the combination of several features in compound **1** that make this structure special: (i) both the water layer and the coordination compound form a two-dimensional polymer, (ii) the water layer has a relatively planar structure, and (iii) there is no direct bonding interaction between the water molecules and the imidazolium salt and only one strong hydrogen bond per asymmetric unit between the different layers.

Compound **1** is stable in air with the water molecules between the layers being trapped at room temperature, although analysis by DSC shows that loss of water begins already above 40 °C. If **1** is heated under vacuum at 100−110 °C, the water molecules are completely removed after several minutes. In D_2O, only four magnetically different carbon nuclei are observed by ^{13}C NMR spectroscopy, which strongly suggests that **1** exists in solution as solvated cation and anion. Electrospray ionization mass spectrometry (ESI-MS) offers supporting information for this proposition but also provides clues to the growth of the extended coordination structure. At low concentration, ca. <1 ppm, only the imidazolium moiety $[C_7H_7N_2O_4]^+$ is observed. As the concentration is increased to 5−10 ppm, various aggregates are observed, which on the basis of their isotopic pattern were assigned, among others, to species of the composition $[(C_7H_7N_2O_4)_4Sr_3]^{2+}$, $[(C_7H_7N_2O_4)_6Sr_4]^{2+}$, and $[(C_7H_7N_2O_4)_8Sr_5]^{2+}$. The size of the aggregates increases further with increasing concentration, but their relative intensity remains low. It is not unreasonable to assume that this growth in aggregate size represents the early stages of the nucleation process prior to the onset of crystallization.

Acknowledgment. We thank the EPFL and Swiss National Science Foundation for financial support.

Supporting Information Available: Experimental procedures, crystallographic information (cif) and additional representations of the structure. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0504238

---

(16) (a) Park, K.-M.; Kuroda, R.; Iwamoto, T. *Angew. Chem., Int. Ed.* **1993**, *32*, 884. (b) Dahlems, T.; Mootz, D.; Schilling, M. *Z. Naturforsch. B* **1996**, *51*, 536. (c) Albert, A.; Mootz, D. *Z. Naturforsch. B* **1997**, *52*, 615.

(17) (a) de Pablo, L.; Chávez, M. L.; Sum, A. K.; de Pablo, J. J. *J. Chem. Phys.* **2004**, *120*, 939. (b) de la Calle, C.; Suquet, H. *Rev. Mineral.* **1988**, *19*, 455.