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2:1 Cocrystals of Homochiral and Achiral Amino Acid Zwitterions with Li^+ Salts: Water-Stable Zeolitic and Diamondoid Metal−Organic Materials

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Supporting Information

ABSTRACT: Eight 2:1 cocrystals of amino acid zwitterions and Li^+ salts were crystallized from hot water to afford cationic networks based on tetrahedral lithium cations: square grids, an ABW topology net, and diamondoid nets.

The global economy utilizes millions of tons per year of synthetic crystalline microporous inorganic zeolites for applications such as petrochemical cracking, ion-exchange for water softening and purification, and gas separations. Synthetic inorganic zeolites typically consist of oxide anions that link tetrahedral aluminum or silicon cations (nodes or primary building units, PBUs) in a 2:1 ratio.[1] The key to the existence of microporosity in zeolites is that the oxide linkers are angular (M−O−M angles typically range from 140° to 165°), thereby facilitating the generation of a wide range of topologies that are based on rings, fused rings (secondary building units, SBUs), and polyhedral cages (complex building units, CBUs). Which particular topology exists for a given chemical composition is typically controlled by reaction conditions, counterions, and/or structure-directing agents[2] (SDAs). The absence of counterions or SDAs or the use of a linear linker more typically manifests the tetrahedral node in the form of a diamondoid (**dia**) net[3,4] that, unlike most zeolites, can readily interpenetrate to mitigate the creation of free space.

The ground rules for generating zeolitic and/or **dia** networks are therefore self-evident and have been validated across a remarkably diverse range of tetrahedral PBUs (e.g., phosphates,[5] transition metal cations,[6−8] metal clusters[9]) and linkers (including purely organic ligands that form coordination bonds[10] or hydrogen bonds[11−13]). Coordination polymers that form zeolitic structures with extra-large porosity, zeolitic metal−organic materials, are exemplified by zeolitic imidazolate frameworks[14−16] (ZIFs), boron imidazolate frameworks[17] (BIFs), zeolite-like metal−organic frameworks[18] (ZMOFs), and the zeolite NPO sustained by metal−carboxylate clusters only (denoted as crystalline porous material, CPM).[19] ZIFs are based on imidazolate ligands that subtend an angle of ~145°, whereas the prototypal ZMOFs use 4,5-imidazoledicarboxylate[20] and pyrimidine-based ligands[21,22] in the presence of SDAs to coordinate to eight-coordinate metals such as In and Cd. BIFs are inherently of low density because they are based on tetrahedral boron atoms. That low density is a desirable property means that lithium, the lightest metal in the periodic table, is a particularly attractive target to serve as a tetrahedral node in either zeolitic or **dia** networks. Furthermore, lithium forms many air- and water-stable coordination environments, and not all existing zeolitic metal−organic materials are water stable. In this context, a prototypal structure was reported by Pinkerton et al., who isolated a lithium-based zeolitic ABW network with a hexachlorotantalum anion embedded in what was described as a three-dimensional Li−Cl−dioxane network.[23] However, this compound is extremely moisture sensitive. Feng and co-workers addressed the challenge elegantly by employing both lithium and boron with imidazolates in BIF-9-Li, a compound with RHO topology,[24] and combined lithium with 4-pyridinol to target cubane clusters, leading to a porous lithium−organic framework with ACO topology.[25] Other approaches to low-density porous materials based on lithium include the following: Robson et al. reported a microporous lithium isonicotinate with square channels;[26] Henderson and co-workers isolated a pillared bilayer and a diamondoid net with solvated lithium aryloxides;[27] Parise et al. reported a MOF based on lithium and 2,5-pyridinedicarboxylic acid that loses porosity upon solvent removal.[28] In this Communication, we describe a new and general strategy to build lithium-based zeolitic metal−organic materials (LiZMOMs) and lithium-based diamondoid metal−organic materials (LiDMOMs) by exploiting the Li−carboxylate−Li linkages that can be formed when amino acid zwitterions form cocrystals with lithium salts.

The strategy described herein is based on generating compounds in which there is a stoichiometric ratio of one lithium cation and two carboxylate anions. That carboxylate moieties can sustain **dia** nets is exemplified in a series of divalent metal formates that naturally possess the required 2:1 ratio of linker to node.[29,30] Indeed, such structures can even exhibit the rarely encountered lonsdaleite[31,32] (**lon**) topology. However, that lithium is monovalent means that the requisite 2:1 ratio of linker to node will be very difficult to achieve with anionic linkers. Bu and co-workers circumvented this issue by supplementing neutral lithium imidazolates with neutral bifunctional N-donor ligands.[33] We have addressed this problem by using the carboxylate moieties in amino acids zwitterions to serve as linkers between two lithium cations. We are in effect targeting a new class of compound: 2:1 cocrystals of amino acid zwitterions and inorganic lithium salts. The use of amino acids to form coordination polymers[34,35] is already established and provides numerous opportunities: (1) Many amino acids are commercially available,

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and they are typically inexpensive. (2) Figure 1 reveals that Li—carboxylate—Li angles offer the requisite diversity needed to generate a wide range of extended structures. The remarkable range of Li—carboxylate—Li angles stems at least partly from the tendency of the carboxylate ligand to exhibit either endodentate or exodentate bridging modes. (3) The Li—carboxylate bond is robust even in the presence of water. (4) Amino acids possess functionalized side chains that facilitate presynthetic fine-tuning of the resulting structures. (5) The use of a homochiral amino acid means that a homochiral crystal is guaranteed. (6) The lack of a center of inversion in the tetrahedral node and Li—carboxylate—Li linker means that even achiral amino acids might generate chiral or polar structures if a 3D net is formed. (7) Many amino acids are soluble in water, facilitating "green" synthesis. (8) The charge of the network is inverted compared to that of zeolites because the framework is cationic and the required counterions are anions; i.e., anion-exchange becomes feasible.

In principle, 2:1 cocrystals of amino acids and lithium salts therefore fit the criteria for formation of **dia** and/or zeolitic frameworks with chiral or polar structures. However, another structural feature of zeolites is the presence of one or more rings, typically four-, six-, or eight-connected M_nO_n rings. Four-connected $Li_4(carboxylate)_4$ rings have previously been observed in a 2:1 cocrystal of glycine and lithium nitrate demonstrating a square grid network[37] (Refcode ROZTUW, Li—C—Li angles 115.88° and 117.83°). With the structural prerequisites for self-assembly of zeolitic and/or **dia** networks in mind, we have prepared a series of 2:1 amino acid (sarcosine, SAR; *N,N*-dimethylglycine, DMG; betaine, BTN; and L-proline, PRO) cocrystals of lithium salts (lithium chloride, LIC; lithium bromide, LIB; and lithium nitrate, LIN). Cocrystals of the desired stoichiometry were prepared by slow evaporation of concentrated aqueous solutions of LIC, LIB, or LIN and 2 equiv of the amino acid at ~80 °C. The resulting cocrystals are thermally stable to at least 200 °C and are readily soluble in water, although less soluble than the parent LiX salts. Crystallographic analysis of the products revealed three distinct networks or supramolecular isomers: square grids based on only four-connected $Li_4(carboxylate)_4$ rings; diamondoid networks based on only six-connected $Li_6(carboxylate)_6$ rings; and a zeolitic ABW network based on four-, six-, and eight-connected $Li_n(carboxylate)_n$ (n = 4, 6, and 8) rings.

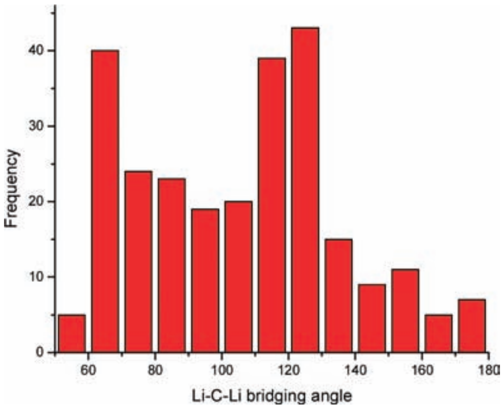

Figure 1. Distribution of the Li—C—Li angle in crystal structures that contain lithium cations bridged by carboxylate moieties (data obtained using CSD[36] version 5.31).

LICSAR2 and LINBTN2 form square grids, as illustrated in Figure 2a. Each lithium cation is bridged by four carboxylate moieties [Li—O distances: 1.905(3), 1.916(3), 1.928(3), and 1.966(3) Å for LICSAR2; 1.931(3), 1.933(3), 1.958(3), and 1.973(3) Å for LINBTN2] to form an undulating square grid, while the tails of the amino acids point away (above and below) from the square grid to establish a bilayer packing arrangement. The chloride and nitrate anions are surrounded by hydrogen bond donors, N—H···Cl [3.1011(1), 3.1549(1) Å] and C—H···O [3.154(2)—3.606(2) Å] interactions, respectively. These square cavities are ~5.0 Å × 6.0 Å (LICSAR2) and 5.5 Å × 5.7 Å (LINBTN2) and are part of undulating sheets that stack in a roughly eclipsed manner.

Lithium-sustained **dia** nets (LiDMOMs) are exemplified by LICDMG2, LIBDMG2, LICPRO2, LIBPRO2, and LINPRO2-(dia), as illustrated in Figure 2b. Each lithium cation is bridged by four carboxylate anions [Li—O distances: 1.898(3) and 1.910(3) Å for LICDMG2; 1.908(3) and 1.942(3) Å for LIBDMG2; 1.9341(18) and 1.9536(19) Å for LICPRO2; 1.939(2) and 1.974(3) Å for LIBPRO2; 1.937(9), 1.952(9), 1.955(9), and 1.956(9) Å for LINPRO2] to form a cationic **dia** net with hexagonal channels exhibiting diameters ranging from 10.1 to 12.6 Å. The counterions reside in these channels, the diameters of which are about twice that of β-cristobalite (5.9 Å). In each **dia** net, the framework is reinforced by charge-assisted hydrogen bonding [LICDMG2, 2.742(2) Å; LIBDMG2, 2.747(2) Å; LICPRO2, 2.7404(15) Å; LIBPRO2, 2.737(2) Å; LINPRO2,

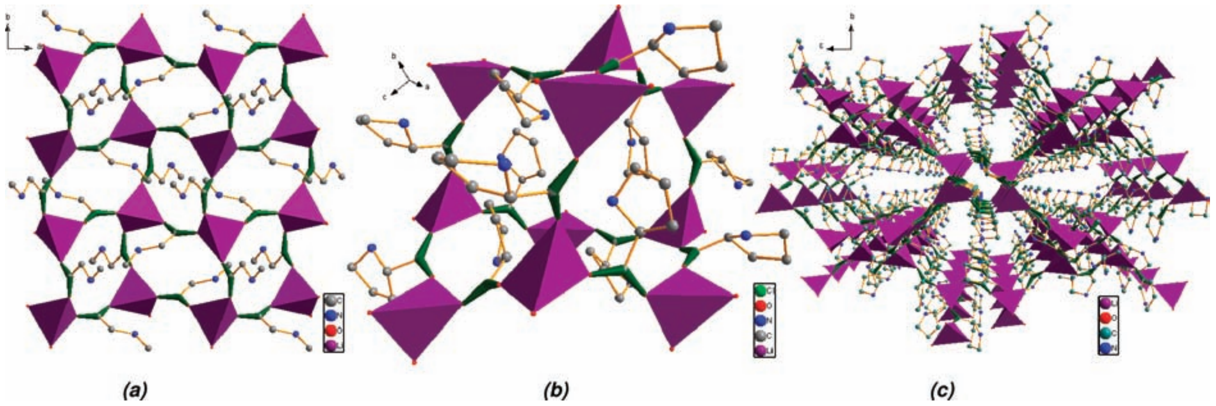

Figure 2. Structural diversity in the networks formed by 2:1 cocrystals of amino acids with lithium salts: (a) square grids, (b) diamondoid LiDMOM nets, and (c) zeolitic ABW topology in the first LiZMOM. Hydrogen atoms and counteranions are omitted for clarity.

2.751(5) and 2.762(5) Å] between the carboxylate of one amino acid and the ammonium of an adjacent amino acid. **Dia** nets are prone to interpenetration, but the presence of pairs of counterions and the bulkiness of the amino acid substituents precludes interpenetration in the LiDMOMs reported herein. The use of L-proline means that its crystal structures exist in chiral space groups: LICPRO2 and LIBPRO2 crystallize in $P4_12_12$, whereas LINPRO2(dia) crystallizes in $P2_12_12_1$. However, a one-fold **dia** net cannot accommodate a center of inversion if the linker does not possess a center of inversion; therefore, LICDMG2 and LIBDMG2 must also crystallize in noncentrosymmetric space groups, in this case the polar space group *Fdd*2.

The first example of lithium carboxylate chemistry leading to a lithium-sustained zeolitic net (LiZMOM) is a polymorph of LINPRO2 which exists as an ABW net, as illustrated in Figure 2c. A combination of $Li_4(carboxylate)_4$ and $Li_8(carboxylate)_8$ rings generate channels that lie parallel to the crystallographic *a* axis. When viewed down the crystallographic *c* axis, the presence of $Li_6(carboxylate)_6$ rings is evident. Li—O bond distances in the range of 1.913(3)—1.976(3) Å occur in the four- and eight-connected rings, while Li—O bond distances in the range 1.920(2)—1.976(3) Å are observed in the six-connected rings. Pairs of nitrate anions occupy the eight-connected ring channels, and they are crystallographically ordered through N—H···O hydrogen-bonding interactions [2.735(8), 2.885(8), 3.005(8) Å]. The dimensions of the largest eight-connected ring channel are about twice those of an ABW zeolite (Figure 3). ABW topology was reported in one of the first synthetic zeolites as detailed by Barrer and White in 1951.[38] They used the term "Li-A" to describe the new structure, but the authors' initials were subsequently used when "ABW" was coined to define this topology. Although the ABW form of LINPRO2 is stable at elevated temperatures, it converts to the diamondoid form, LINPRO2(dia), upon standing in mother liquor under ambient conditions. Grinding of the plate-like crystals of LINPRO2-(ABW) also results in conversion to LINPRO2(dia), as determined by powder X-ray diffraction. ABW zeolite has been observed as an intermediate phase in zeolite synthesis.[39]

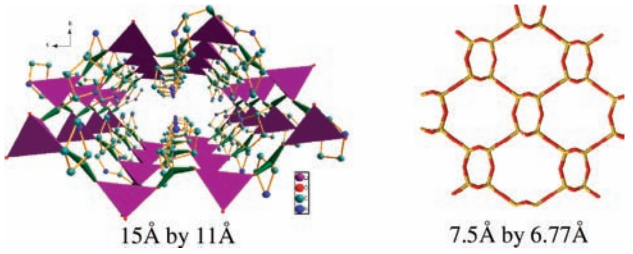

Figure 3. Significant expansion of structure occurs in LINPRO2 vs the prototypal ABW zeolite because of the ditopic carboxylate linker.

Table 1. Analysis of Li—C—Li Angles (deg) Forming Four-, Six-, and Eight-Connected Ring Motifs

	4-connected	6-connected	8-connected
LICSAR2	117.78, 157.08		
LINBTN2	122.77, 144.37		
LICDMG2		153.27	
LIBDMG2		153.27	
LICPRO2		156.00	
LIBPRO2		155.50	
LINPRO2(dia)		154.84, 158.77	
LINPRO2(ABW)	122.13, 148.72	148.72, 155.18, 158.97	122.13, 148.72, 155.18, 158.97
ABW	149.4, 156.8	156.8, 156.9°, 180	149.4, 180

Whereas the Li—carboxylate bond distances observed in the structures reported herein exhibit a relatively narrow range, the Li—carboxylate—Li angles range from 117.78° [$Li_4(carboxylate)_4$ ring in LICSAR2] to 158.97° [$Li_8(carboxylate)_8$ ring in LINPRO2(ABW)] and are detailed in Table 1. The majority of angles cluster around 150°, intermediate between those for linear and tetrahedral geometry, which is consistent with what would be needed to form a wider range of zeolitic structures. In conclusion, we have demonstrated that 2:1 cocrystals of amino acids with lithium salts generate square grids, **dia** nets, and the first LiZMOM, which exhibits ABW topology. Given that NH groups exhibit affinity toward CO_2, as demonstrated in a recently reported microporous NH(adenine)-tethered MOF,[40] it is possible that the abundance of ammonium groups in the structures reported herein could lead to a role in carbon capture[41−43] or anion recognition. However, the nets reported herein are densely packed, and preliminary ion-exchange experiments failed. The approach described herein, which relies upon one-step synthesis from readily available starting materials, should be general because of the modular nature of the structure and the ready availability of amino acids and counteranions. Future studies will focus upon larger anions and/or templates and, given the expected diversity of Li—carboxylate—Li angles, we envisage a range of LiZMOMs that parallels the structural diversity seen in inorganic zeolites and zeolitic metal—organic materials.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthetic procedures and solid-state characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Baerlocher, C.; McCusker, L. B.; Olson, D. H. *Atlas of Zeolite Framework Types*, 6th revised ed.; Elsevier Science: Amsterdam, 2007.
(2) Cundy, C. S.; Cox, P. A. *Chem. Rev.* **2003**, *103*, 663.
(3) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283.
(4) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176.
(5) Davis, M. E. *Nature* **2002**, *417*, 813.
(6) Lopez, S.; Kahraman, M.; Harmata, M.; Keller, S. W. *Inorg. Chem.* **1997**, *36*, 6138.
(7) Evans, O. R.; Lin, W. B. *Acc. Chem. Res.* **2002**, *35*, 511.
(8) Keller, S. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 247.
(9) Liang, K.; Zheng, H. G.; Song, Y. L.; Lappert, M. E.; Li, Y. Z.; Xin, X. Q.; Huang, Z. X.; Chen, J. T.; Lu, S. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 5776.
(10) Fang, Q.; Zhu, G.; Xue, M.; Sun, J.; Wei, Y.; Qiu, S.; Xu, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3845.
(11) Copp, S. B.; Holman, K. T.; Sangster, J. O. S.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 2233.

(12) Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 8719.

(13) Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1078.

(14) Hayashi, H.; Cote, A. P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Nat. Mater.* **2007**, *6*, 501.

(15) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186.

(16) Huang, X. C.; Lin, Y. Y.; Zhang, J. P.; Chen, X. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1557.

(17) Zhang, J.; Wu, T.; Zhou, C.; Chen, S.; Feng, P.; Bu, X. *Angew. Chem.* **2009**, *121*, 2580.

(18) Liu, Y.; Kravtsov, V. C.; Larsen, R.; Eddaoudi, M. *Chem. Commun.* **2006**, 1488.

(19) Zheng, S.-T.; Zuo, F.; Wu, T.; Irfanoglu, B.; Chou, C.; Nieto, R. A.; Feng, P.; Bu, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 1849.

(20) Alkordi, M. H.; Brant, J. A.; Wojtas, L.; Kravtsov, V. C.; Cairns, A. J.; Eddaoudi, M. *J. Am. Chem. Soc.* **2009**, *131*, 17753.

(21) Navarro, J. A. R.; Barea, E.; Salas, J. M.; Masciocchi, N.; Galli, S.; Sironi, A.; Ania, C. O.; Parra, J. B. *Inorg. Chem.* **2006**, *45*, 2397.

(22) Sava, D. F.; Kravtsov, V. C.; Nouar, F.; Wojtas, L.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, *130*, 3768.

(23) Hasche, S.; Mock, C.; Otto, J.; Schweppe, F.; Kirschbaum, K.; Krebs, B.; Pinkerton, A. A. *Inorg. Chim. Acta* **2000**, *298*, 9.

(24) Wu, T.; Zhang, J.; Zhou, C.; Wang, L.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2009**, *131*, 6111.

(25) Zhao, X.; Wu, T.; Zheng, S.-T.; Wang, L.; Bu, X.; Feng, P. *Chem. Commun.* **2011**, *47*, 5536.

(26) Abrahams, B.; Grannas, M.; Hudson, T.; Robson, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 1087.

(27) Morris, J. J.; Noll, B. C.; Henderson, K. W. *Cryst. Growth Des.* **2006**, *6*, 1071.

(28) Banerjee, D.; Kim, S. J.; Li, W.; Wu, H.; Li, J.; Borkowski, L. A.; Philips, B. L.; Parise, J. B. *Cryst. Growth Des.* **2010**, *10*, 2801.

(29) Saravanan, K.; Nagarathinam, M.; Balaya, P.; Vittal, J. J. *J. Mater. Chem.* **2010**, *20*, 8329.

(30) Wang, Z. M.; Zhang, B.; Fujiwara, H.; Kobayashi, H.; Kurmoo, M. *Chem. Commun.* **2004**, 416.

(31) Sreenivasulu, B.; Vittal, J. J. *Cryst. Growth Des.* **2003**, *3*, 635.

(32) Chen, Z. L.; Jiang, C. F.; Yan, W. H.; Liang, F. P.; Batten, S. R. *Inorg. Chem.* **2009**, *48*, 4674.

(33) Zheng, S.-T.; Li, Y.; Wu, T.; Nieto, R. A.; Feng, P.; Bu, X. *Chem.—Eur. J.* **2010**, *16*, 13035.

(34) Anokhina, E. V.; Jacobson, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 3044.

(35) Vaidhyanathan, R.; Bradshaw, D.; Rebilly, J.-N.; Barrio, J. P.; Gould, J. A.; Berry, N. G.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6495.

(36) Allen, F. *Acta Crystallogr., Sect. B* **2002**, *58*, 380.

(37) Baran, J.; Drozd, M.; Ratajczak, H.; Pietraszko, A. *J. Mol. Struct.* **2009**, *927*, 43.

(38) Barrer, R. M.; White, E. A. D. *J. Chem. Soc.* **1951**, 1267.

(39) Aiello, R.; Barrer, R, M.; Kerr, I. S. In *Molecular Sieve Zeolites I*; American Chemical Society: Washington, DC, 1974; Vol. 101, p 44.

(40) Stylianou, K. C.; Warren, J. E.; Chong, S. Y.; Rabone, J.; Bacsa, J.; Bradshaw, D.; Rosseinsky, M. J. *Chem. Commun.* **2011**, *47*, 3389.

(41) Holloway, S. *Energy* 2005, *30*, 2318.

(42) Arenillas, A.; Smith, K. M.; Drage, T. C.; Snape, C. E. *Fuel* **2005**, *84*, 2204.

(43) Lackner, K. S. *Science* **2003**, *300*, 1677.