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Inorganic Chemistry Article

Two Coordination Polymers Created via In Situ Ligand Synthesis Involving C–N and C–C Bond Formation

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We report the synthesis and crystal structures of two transition metal-based coordination polymers comprising ligand molecules not included in the original reaction mixtures but instead formed in situ during hydrothermal treatment. Zinc *meso*-iminodisuccinate hydrate (**I**), $Zn_2(C_8H_7NO_8)\cdot 0.57H_2O$, formed from zinc acetate and L-aspartic acid, and tetraaquanickel(II) 5,10-dioxo-5,10-dihydro-4,9-dioxa-pyrene-2,7-dicarboxylate (**II**), $Ni(H_2O)_4(C_{16}H_4O_8)$, formed from nickel acetate and 5-hydroxyisophthalic acid. We show that the formation of **I** takes place via a fumaric acid intermediate, while the formation of **II** requires the formation of a new C–C bond. The structure of **I** consists of weakly interacting sheets, while the structure of **II** consists of strongly hydrogen-bonded chains. Crystal data: for **I**, $P2_1/n$ (14), $a = 10.073$ Å, $b = 9.894$ Å, $c = 12.053$ Å, $\beta = 105.605°$, $V = 1156.87(13)$ Å^3, $Z = 4$; for **II**, $P\bar{1}$ (2), $a = 5.011$ Å, $b = 6.526$ Å, $c = 12.305$ Å, $\alpha = 76.868°$, $\beta = 84.988°$, $\gamma = 87.619°$, $V = 390.3(4)$ Å^3, $Z = 1$.

Introduction

The structural and functional diversity of coordination polymers has brought these materials wide attention in recent years.[1] A large number of structures reported to date have been prepared hydrothermally or solvothermally, in the temperature range of 100−250 °C. In most cases, the ligand molecule included in the starting mixture is incorporated directly into the resultant framework structure. However, in superheated solution conditions, unusual chemical changes to the ligand molecule itself can occur, some of which are previously unreported in the organic chemical literature. In the case of the 4-cyclohexene-1,2-dicarboxylate frameworks studied by Lee et al. and Kim et al.,[2] sufficiently high temperatures lead to *cis*−*trans* ring isomerism in the ligand molecules, yielding frameworks of the new isomer. Examples in the literature exist in which ligand functional groups are added,[3] removed,[4] or changed[5] and in which ligand molecules are cleaved[6] or condense with other molecules that are present.[7] In other cases, a ligand may undergo carbon−carbon bond rearrangement to form a previously unknown organic molecule; Abrahams et al.[8] have reported a case in which dihydroxyfumaric acid rearranges to form the fully deprotonated conjugate base of hydroxymethanetricarboxylic acid, which in the presence of several transition metals yields highly symmetric octanuclear complexes.

Here we report the synthesis of two coordination polymers of transition metals with ligand molecules that are dimers of the starting ligands. Zinc *meso*-iminodisuccinate (IDS) hydrate (**I**) was synthesized from zinc acetate and L-aspartic acid, and tetraaquanickel(II) 5,10-dioxo-5,10-dihydro-4,9-dioxa-pyrene-2,7-dicarboxylate (DDPD) (**II**) was synthesized from nickel acetate and 5-hydroxyisophthalic acid. The stoichiometry of **I** differs from that of its starting mixture because of the ligand dimerization.

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While several frameworks of aspartate[9] and several of 5-hydroxyisophthalate[10] are known, the structures reported here of the dimeric acids are different. A nickel complex of *meso*-iminodisuccinic acid has been reported by Poznyak et al.,[11] but the structure is molecular. A dimerization similar to that in **I** was reported by Zhang et al.,[12] who synthesized cadmium *meso*-oxidisuccinate (the ether analog to the secondary amine in iminodisuccinate) from cadmium sulfate and malic acid.

To our knowledge, 5,10-dioxo-5,10-dihydro-4,9-dioxapyrene-2,7-dicarboxylic acid itself is unreported; a CAS number search on the structure failed. Its ring system is identical to that of the natural tetracyclic diester ellagic acid. Similar molecules with various other groups at the 2- and 7-positions, such as $-NH_2$, $-X$, $-CN$, $-NHAc$, $-OH$, $-OAc$, and $-NO_2$, were reported by Migachev.[13]

Experimental Section

Materials. All reagents were used as purchased; $Zn(ac)_2{\cdot}2H_2O$, $Ni(ac)_2{\cdot}4H_2O$, and 5-hydroxyisophthalic acid were from Aldrich, and L-aspartic acid was from Acros. Syntheses were carried out in Parr Teflon-lined stainless steel autoclaves under autogenous pressure.

Synthesis of I, $Zn_2(C_8H_7NO_8){\cdot}0.57H_2O$. Colorless pyramidal crystals (0.4 × 0.3 × 0.2 mm) of **I** were synthesized by combination of 1 mmol (219 mg) of $Zn(ac)_2{\cdot}2H_2O$ (98+%) and 1 mmol (133 mg) of L-aspartic acid (98+%) with 5 mL of deionized water. This mixture was sealed in a 23 mL autoclave and heated at 180 °C for 2 days. The reaction vessel was cooled at room temperature, and the product was washed with deionized water and vacuum filtered. At temperatures of 125 °C or less, no solid is produced, and at 150 °C, phase-pure polycrystalline clusters are produced in approximately 50% yield. Attempts to synthesize analogs using other divalent metals of similar ionic radius (Mg, Mn, Co, and Ni) failed, yielding only an amorphous solid, as did attempts to produce a similar adduct ligand from glutamic acid. The use of racemic DL-aspartic acid instead of l-aspartic acid yields identical products, which suggests that racemization occurs in the superheated solution. Powder diffractometry was performed on a Phillips X'Pert diffractometer equipped with Cu Kα radiation ($\lambda = 1.5418$ Å) and a Phillips X'Celerator array detector, and the diffraction pattern matched that simulated from the single-crystal structure determination (see Supporting Information). Elemental analysis (C, H, N) was carried out by the Marine Sciences Institute Analytical Laboratory at UCSB. Found (wt. %): H, 2.11; C, 24.58; N, 3.51. Calcd (wt. %): H, 2.12; C, 24.88; N, 3.63.

Table 1. Crystal Data and Structure Refinement Parameters

	zinc *meso*-IDS hydrate **I**	tetraaquanickel(II) DDPD **II**
empirical formula	$Zn_2(C_8H_7NO_8){\cdot}xH_2O$ ($x = 0.57(1)$)	$Ni(H_2O)_4(C_{16}H_4O_8)$
fw	386.20	454.97
temp (K)	298(2)	298(2)
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	10.0725(7)	5.011(3)
b (Å)	9.8937(6)	6.526(3)
c (Å)	12.0531(8)	12.305(7)
α (deg)	90	76.868(8)
β (deg)	105.6050(10)	84.988(8)
γ (deg)	90	87.619(8)
vol (Å^3)	1156.87(13)	390.3(4)
Z	4	1
density (calcd) (g/cm^3)	2.217	1.936
abs coeff (mm^{-1})	4.189	1.320
F_{000}	767	232
cryst size (mm)	0.4 × 0.3 × 0.2	0.7 × 0.4 × 0.05
θ range	2.35−27.48°	1.70−26.33°
index ranges	$-13 \le h \le 12$, $-12 \le k \le 9$, $-15 \le l \le 15$	$-6 \le h \le 6$, $-8 \le k \le 8$, $-15 \le l \le 15$
reflns collected	6705	3083
independent reflns	2557 [$R_{int} = 0.0213$]	1506 [$R_{int} = 0.0500$]
completeness to $\theta = 27.48°$	96.6%	94.7%
abs correction	SADABS	empirical
refinement method	full-matrix least-squares on $\lvert F\rvert^2$	full-matrix least-squares on $\lvert F\rvert^2$
data/restraints/params	2557/3/192	1506/0/133
GOF on $\lvert F\rvert^2$	1.025	1.070
final R indices [$I > 2\sigma(I)$]	R1 = 0.0241, wR2 = 0.0615	R1 = 0.0469, wR2 = 0.1196
final R indices [all data]	R1 = 0.0304, wR2 = 0.0643	R1 = 0.0532, wR2 = 0.1241
largest diff. peak and hole	0.680 and −0.295 e/Å^3	0.909 and −0.609 e/Å^3

Synthesis of II, $Ni(H_2O)_4(C_{16}H_4O_8)$. Orange sheet crystals (0.7 × 0.4 × 0.05 mm) of **II** were synthesized by heating 1.00 g of $Ni(ac)_2{\cdot}4H_2O$ (98%), 725 mg of 5-hydroxyisophthalic acid (97%), and 50 mL of deionized water in a 125 mL autoclave at 150 °C for 2 days. The reaction vessel was cooled at room temperature, and the product was washed with deionized water and vacuum filtered. The synthesis was very sensitive to experimental conditions, possibly being affected by other variables which could not be ascertained. Elemental analysis, TGA, and powder diffractogram are not available because a phase-pure sample of **II** was not synthesized. The yield of the impure product was approximately 25%. Synthesis attempts with other metals yielded only amorphous solid.

Structure Determinations. Suitable single crystals of **I** and **II** were selected under a polarizing microscope and glued to glass fibers. Intensity data were collected at room temperature on a Siemens SMART CCD diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). The structures were solved using direct methods and difference Fourier synthesis and were refined against $|F|^2$ using the *SHELXTL* software package.[14] Absorption corrections for **I** were made using *SADABS*,[15] and those for **II** were made via a ψ-scan performed in the *XPREP* module of *SHELXTL*. The extinction coefficients both refined to within three esd's of zero and were thus removed from the refinements. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically, with thermal parameters equal to 1.2 times those of the

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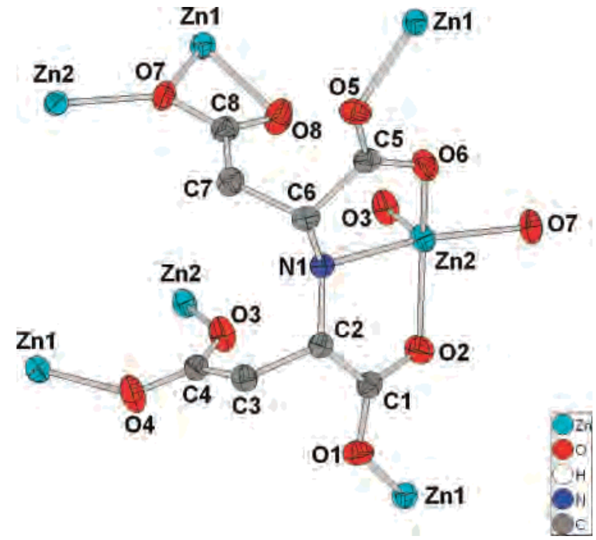


Figure 1. Thermal ellipsoid plot (50% probability) of one iminodisuccinate (IDS) anion in zinc IDS hydrate **(I)** and the seven zinc cations to which it coordinates.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **I**[a]

Zn(1)−O(5)	1.9604(16)	Zn(2)−O(3)#4	2.0006(16)
Zn(1)−O(1)#2	1.9794(15)	Zn(2)−O(6)	2.0506(17)
Zn(1)−O(8)#3	2.2731(17)	Zn(2)−N(1)	2.1213(18)
Zn(1)−O(7)#3	2.0751(18)	Zn(2)−O(7)#1	2.0066(16)
Zn(1)−O(4)#1	1.9677(18)	Zn(2)−O(2)	2.0667(17)

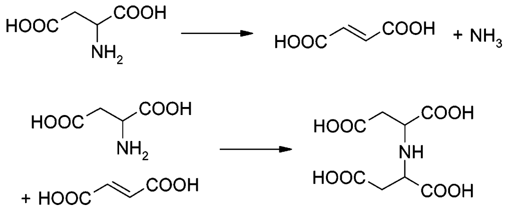
O(5)−Zn(1)−O(4)#1	106.93(8)	O(5)−Zn(1)−O(1)#2	99.60(7)
O(4)#1−Zn(1)−O(1)#2	99.31(7)	O(5)−Zn(1)−O(7)#3	118.16(7)
O(4)#1−Zn(1)−O(7)#3	98.99(7)	O(1)#2−Zn(1)−O(7)#3	130.40(6)
O(5)−Zn(1)−O(8)#3	94.68(7)	O(4)#1−Zn(1)−O(8)#3	155.48(7)
O(1)#2−Zn(1)−O(8)#3	88.06(7)	O(7)#3−Zn(1)−O(8)#3	59.64(6)
O(3)#4−Zn(2)−O(6)	120.57(7)	O(3)#4−Zn(2)−O(7)#1	98.23(7)
O(3)#4−Zn(2)−O(2)	95.86(7)	O(7)#1−Zn(2)−O(6)	93.01(6)
O(6)−Zn(2)−O(2)	140.77(7)	O(7)#1−Zn(2)−O(2)	95.80(6)
O(7)#1−Zn(2)−N(1)	161.80(7)	O(3)#4−Zn(2)−N(1)	99.74(7)
O(2)−Zn(2)−N(1)	79.55(6)	O(6)−Zn(2)−N(1)	80.31(6)
Zn(2)#6−O(7)−Zn(1)#3	121.90(8)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x + 1/2, -y + 1/2, z + 1/2$; #2 $x, y + 1, z$; #3 $-x, -y + 1, -z$; #4 $-x, -y, -z$; #5 $x, y - 1, z$; #6 $x - 1/2, -y + 1/2, z - 1/2$.

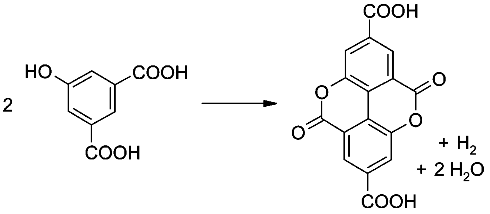
respective mother atoms. For **I**, hydrogens on the iminodisuccinate group were added using a riding model. Those on the water molecule were located in the Fourier difference map and restrained to within 0.8 Å of the oxygen atom and within 1.3 Å of each other. For **II**, phenyl hydrogens were added using a riding model, and water hydrogen positions were refined normally. It was noted initially that the thermal ellipsoid for the water oxygen in **I** was unusually large, so partial occupancy was considered. Values for R1 were higher (∼0.030 for $I > 2\sigma(I)$) for a fully hydrated or an anhydrous model than for half-occupancy. A single site occupancy factor for all the atoms of the water molecule refined to a value of 0.57 ± 0.01 (Table 1). For crystallographic data in CIF format, see the Supporting Information.

TGA/DTA Analysis of I. TGA/DTA Analysis was performed in air on a Mettler 851e TG/sDTA up to 600 °C. Temperatures were ramped at 5 °C/min. A gradual mass loss of 3.78% (2.66% expected for loss of partially occupied water molecule), occurred between 200 and 325 °C, accompanied by a very slight endotherm in the DTA trace. Between 375−500 °C, a further mass loss of 54.1% occurred, with a large corresponding exotherm in the DTA. After both events, 42.4% of the original mass remained (42.2% expected for complete transformation to ZnO). See Supporting Information for full data.

Scheme 1. Dimerization of L-Aspartic Acid to Iminodisuccinic Acid via a Postulated Fumaric Acid Intermediate



Scheme 2. Net Dimerization of 5-Hydroxyisophthalic Acid to 5,10-Dioxo-5,10-dihydro-4,9-dioxa-pyrene-2,7-dicarboxylic Acid



Results and Discussion

Structure of I, $Zn_2(C_8H_7NO_8)\cdot0.57\ H_2O$. Zinc *meso*-iminodisuccinate hydrate, **I**, crystallizes in the space group $P2_1/n$, and consists of sheets running perpendicular to the **n** direction [1 0 -1]. Hydrogen-bonding between the sheets appears to be weak at best; unbound water molecules occur in pairs in the intersheet spaces, with $d(\mathrm{OW-OW}) = 3.11$ Å. These pairs lie between two O4 carboxyl oxygens of consecutive sheets, with $d(\mathrm{OW-O4}) = 3.17$ Å, but the water is otherwise in relatively hydrophobic surroundings. The zinc cations are pentacoordinated, with highly distorted trigonal bipyramidal geometries (Figure 1). This coordination geometry has been well-attested in zinc compounds, including in its coordination polymers, where trigonal pyramidal and tetrahedral zinc cations can be found together in the same structure.[16] This unusual coordination geometry is unfavorable for many other metals, and their failure to form isomorphs under similar conditions may be in part caused by it. The asymmetric unit contains a *meso*-IDS group, a water molecule, and two crystallographically unique zinc cations. (It should be noted not only that (*R*,*R*)- or (*S*,*S*)-IDS groups are incompatible with the packing requirements of **I** but also that the absolute configurations are likely fluxional in the superheated solution.) Zn1 sits in a ZnO_5 polyhedron, with one distant oxygen at 2.27 Å, and Zn2 sits in a ZnO_4N polyhedron, with the nitrogen slightly distant at 2.12 Å (Table 2). All other ligand oxygen atoms lie at distances between 1.96 and 2.08 Å. Pairs of zinc polyhedra (ZnO_4N-ZnO_5) share one corner through O7 to form dimers. Thus the structure contains only finite Zn−O−Zn connectivity, and no Zn−N−Zn connectivity. Unusually, this compound contains no aqua ligands, only uncoordinated waters of hydration; each iminodisuccinate group fully satisfies the coordination requirements of both zinc cations in its formula unit. This type of behavior has been observed in framework

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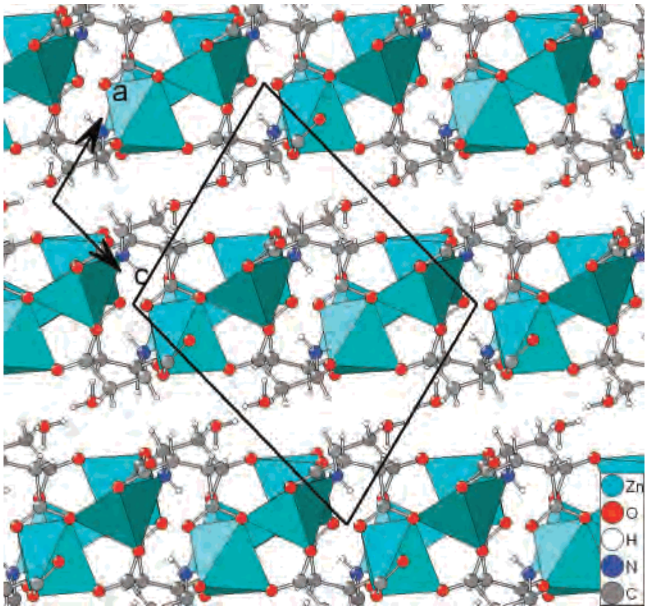

Figure 2. Dimeric arrangement of irregular ZnO_5 and ZnO_4N polyhedra in the two-dimensional structure of zinc IDS hydrate **(I)**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **II**[a]

Ni(1)−O(6)#1	2.062(2)	O(2)−C(3)	1.208(4)
Ni(1)−O(5)#1	2.076(2)	O(4)−C(8)	1.272(4)
Ni(1)−O(4)#1	2.077(2)	O(1)−C(2)	1.389(4)
O(3)−C(8)	1.248(4)	C(3)−C(4)	1.475(5)
O(1)−C(3)	1.380(4)	C(7)−C(1)#2	1.410(4)
C(5)−C(4)	1.406(4)	C(8)−C(7)	1.514(4)
C(1)−C(2)	1.379(4)	C(5)−C(2)#2	1.402(4)
C(6)−C(7)	1.397(5)	C(5)−C(5)#2	1.424(6)
C(6)−C(4)	1.385(5)		
O(6)#1−Ni(1)−O(6)	180.0	C(8)−O(4)−Ni(1)	126.73(19)
O(6)#1−Ni(1)−O(5)#1	89.66(10)	O(6)#1−Ni(1)−O(4)#1	92.38(9)
O(5)#1−Ni(1)−O(5)	180.0	O(5)#1−Ni(1)−O(4)#1	91.10(10)
O(6)−Ni(1)−O(4)#1	87.62(9)	O(4)#1−Ni(1)−O(4)	180.0
O(5)−Ni(1)−O(4)#1	88.90(10)	O(6)−Ni(1)−O(5)#1	90.34(10)

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*, −*y*, −*z* + 1; #2 −*x* + 2, −*y* + 1, −*z*.

structures with a variety of synthesis temperatures,[17] but the lack of aqua ligands in the first zinc coordination spheres resembles frameworks formed at higher temperatures. However, the structure's overall low dimensionality and lack of an infinite Zn−O−Zn network is more consistent with lower-temperature phases (Figure 2).

Dimerization Mechanism of I. On the basis of extant literature, we postulate that L-aspartic acid dimerizes to iminodisuccinic acid via a butenedioic acid intermediate. Unlike other amino acids, aspartic acid is known to deaminate rather than decarboxylate at high temperatures, yielding ammonia and fumaric acid (*trans*-butenedioic acid),[18] as shown in Scheme 1. The addition of butenedioic acid or its alkali salts to aspartic acid to produce iminodisuccinic acid (IDS) or its salts has been reported by two groups to take place in refluxing aqueous NaOH.[19] While these authors used maleic acid (*cis*-butenedioic acid) rather than fumaric acid,

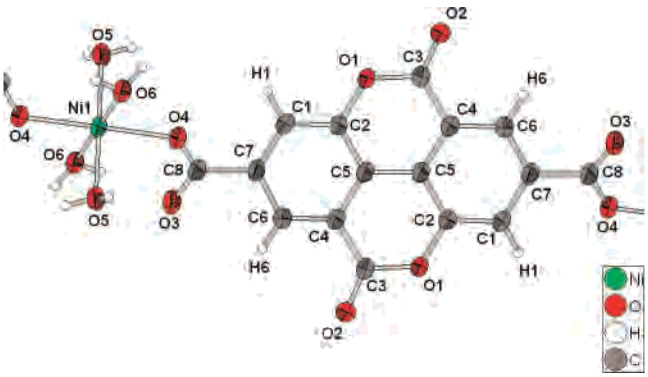

Figure 3. Thermal ellipsoid plot (50% probability) of one formula unit of tetraaquanickel(II) DDPD **(II)**, showing linear chain topology.

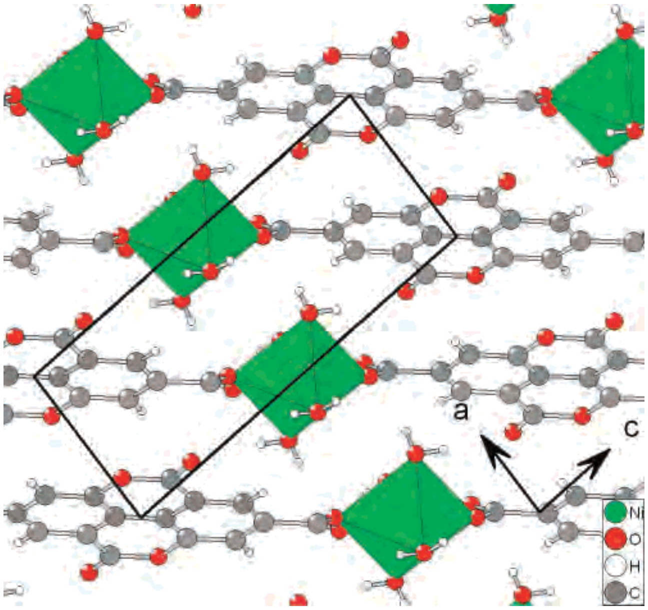

Figure 4. Offset π-stacking of neighboring chains in the structure tetraaquanickel(II) DDPD **(II)**.

it is known that maleic acid readily *cis*−*trans* isomerizes under reflux conditions. Thus, fumaric acid is a likely intermediate in the literature synthesis as well. In their 1993 patent,[19b] Asakawa et al. specifically report the synthesis of the *meso* isomer that is found in the crystal structure of the zinc IDS hydrate we report here. Subsequently, in their 1994 patent, they report another synthesis starting only from maleic acid or maleic anhydride and ammonia.[20]

To confirm the existence of butenedioic acid intermediates, ^1H NMR spectra were taken of solutions of 1 mmol of L-aspartic acid in 5 mL of D_2O, which had been heated in autoclaves to the synthesis temperature of **I** (150 °C) for 2 days, as well as to lower temperatures (100 °C and 125 °C). These spectra exhibited peaks consistent with fumaric acid and maleic acid, as well as peaks consistent with those in the spectrum of a reference iminodisuccinate solution prepared by dissolution of **I** in D_2O with a drop of sulfuric

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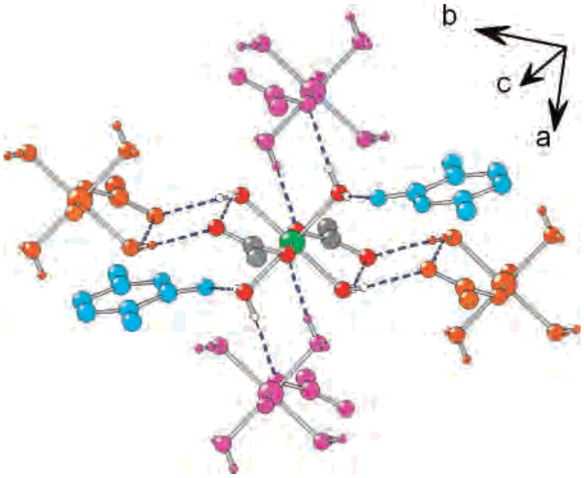

Figure 5. Hydrogen bonds (dotted, dark blue) in tetraaquanickel(II) DDPD **(II)** between the coordination sphere of one Ni(II) cation and portions of six neighboring chains (color coded by symmetry equivalence with respect to the central Ni depicted).

acid at room temperature. Solutions with Zn^{2+} added before heating gave identical spectra to those without Zn^{2+}.

Structure of II, $Ni(H_2O)_4(C_{16}H_4O_8)$. The net dimerization reaction of 5-hydroxyisophthalic acid, which involves the formation of a new C−C bond, is depicted in Scheme 2. Tetraaquanickel(II) DDPD, **II**, crystallizes in the space group $P\bar{1}$, and is a 1-D coordination polymer, with chains running parallel to the [2 1 -1] direction (Figures 3 and 4). Both the nickel cation and the center of the DDPD dianion lie on inversion centers. The DDPD carboxylate groups coordinate to the nickel through only one oxygen atom; the other accepts a hydrogen bond from an aqua ligand. The NiO_6 octahedra are very regular, with d(Ni−O) between 2.062 and 2.077 Å (Table 3). The aqua ligands provide for extensive hydrogen bonding; O−H···O distances range from 2.667 to 2.880 Å, and O−H···O angles from 152.5 to 170.1°. Of the four crystallographically independent H-bonds, one is intrachain and three are interchain. Two of the interchain bonds are close enough to inversion centers to generate H-bond pairs with their symmetry equivalents, and one of these pairs is cross-connected into squares by sharing end atoms with the intrachain bonds. Thus each chain exchanges pairs of H-bonds with its neighbors along one axis [1 0 0], cross-connected pairs with neighbors along a second axis [0 1 0], and single H-bonds with neighbors along a third axis [0 1 1] (see Supporting Information for hydrogen bond parameters for **II**). The DDPD ring systems are packed in a way that provides offset π-stacking (Figure 4), with a perpendicular distance of 3.52 Å and an oblique in-plane translation of roughly the same amount.

We suspect that C−C bond formation in the dimerization of 5-hydroxisophthalic acid proceeds via an *ortho*−*ortho* coupling of phenol radicals. One-electron oxidation of the phenoxide anion of the starting acid, perhaps by O_2, generates corresponding phenol radicals, which preferentially couple at the *ortho* carbons because of steric hindrance around the *para* carbons. Rearomatization to reform the phenol groups, followed by two internal esterifications, yields the product acid.

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Supporting Information Available: Bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, powder diffractogram for **I**, thermal analysis for **I**, and hydrogen bond parameters for **II**. This material is available free of charge via the Internet at http://pubs.acs.org.

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