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Liquid-Assisted Solid-State Reaction: Formation of a Three-Dimensional Hydrogen-Bonded Network and Evidence for Proton Induced Electron Transfer

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ABSTRACT: We describe the first observation of the quantitative and rapid synthesis of a (10,3)-*b* three-dimensional hydrogen bonded network $\{[Ru(H_2biim)_3](TMA)\} \cdot 5H_2O$ ($\mathbf{1 \cdot H_2O}$) (H_2biim = 2,2′-biimidazole; H_3TMA = trimesic acid) via a "liquid-assisted" solid-state reaction approach. The reaction occurs within minutes of grinding together $[Ru(H_2biim)_3](PF_6)_2$ and Na_2HTMA with a few drops of H_2O_2 as an oxidant and solvent, concomitant with a color change from yellow (Ru(II) ion) to blue-green (Ru(III) ion). The characterization of the solid-state product was achieved by a combination of a single crystal obtained via seeding and powder diffraction experiments. To compare with the solid-state reaction, similar reactions were also carried out in an EtOH solution. Two complexes $\{[Ru(H_2biim)_3](TMA)\} \cdot 10H_2O$ ($\mathbf{2 \cdot H_2O}$) and $[Ru(H_2biim)_3](HTMA)$ (**3**) were isolated in the presence of a polypyridine base, such as 2,2-dipyridylamine or 2,2′:6′,2″-terpyridine or 1,10-phenanthroline. Complex **2** is a (6,3) honeycomb two-dimensional hydrogen-bonded network. Complexes **1** and **2** are topological isomers. The formation of multiple robust hydrogen bonds between $[Ru(H_2biim)_3]^{3+}$ and TMA may trigger the proton transfer from H_2biim to TMA, then electron transfer, resulting in Ru(III) status. This may provide an effective approach for the generation of high status metal complexes via supramolecular interactions. Importantly, our experiments suggest that solution crystallization may at times offer more product diversity than grinding.

Introduction

There is great interest in solid-state reactions as they offer potential reduction in environmental contamination and increased convenience associated with the elimination of solvent from synthetic reactions.[1−3] One efficient approach for achieving these reactions is by milling or grinding the solid reactants together. Since the pioneering work of Etter and co-workers,[4] many organic and inorganic compounds have been prepared by the mechanochemical method.[5−8] Recently, there is some evidence to indicate that the addition of minor amounts of a particular solvent to the grinding process, termed "solvent-assisted" mechanochemistry, can result in a dramatic increase in the rate of formation of product.[9,10]

Charge-transfer complexes have been reported in cocrystal formation by solid-state grinding over a century ago[11] and widely applied in the quinhydrone system.[12] However, the observation of a redox reaction for coordination compounds by grinding is relatively rare.[2] Furthermore, the imidazole-like ligand was widely used as one of the proton carriers because the distal deprotonation of the ligand bearing the imidazole-like component reduces the redox potential of metal center.[13−17] Recently, the strategy of second-sphere coordination has been employed to design ionic receptors based on 2,2′-biimidazole (H_2biim) and 2,2′-bibenzimidazole (H_2bbim) complexes.[18−21] The most important feature for such a complex is that the chelating coordination enforces the syn conformation, then engages in robust hydrogen bonding via the externally directed pair of N−H groups of the H_2biim and H_2bbim ligands to the carboxylate group.[22−27] In complexes $[Ru(bpy)_2(L)](PF_6)_2$ (bpy = 2,2′-bipyridine, L = H_2biim and H_2bbim), the formation of dual robust hydrogen bonds between the H_2biim/H_2bbim ligand and the carboxylate group triggers the proton transfer from H_2biim/H_2bbim to the carboxylate group, and turns the color of the complex from yellow to orange brown and then to violet because of the second sphere donor−acceptor interactions between Ru(II)-H_2biim/H_2bbim and anions. Such interaction (deprotonation in H_2biim/H_2bbim ligand) greatly increases the electron density at the Ru(II) center and shifts its oxidation potential to a less positive value.[28] This fact is also confirmed by an electrochemical experiment through deprotonation at a remote site.[13] It is believed that the increased deprotonation at remote sites results in a shift in the redox potentials to much less positive values. This may afford a new method for the preparation of high status metal complexes via modification of the potential. We obtained a complex $\{[Ru(H_2biim)_3](TMA)\} \cdot DMF \cdot 9H_2O$ (H_3TMA = trimesic acid) serendipitously during the complexation of $[Ru(H_2biim)_3](PF_6)_2$ and H_3TMA in a solution of DMF-EtOH at room temperature.[29] The puzzling question is how to oxidize the stable species $[Ru(H_2biim)_3]^{2+}$ (d^6 electron state) to $[Ru(H_2biim)_3]^{3+}$ (d^5 electron state) in the air-exposed solution. Careful examination of its crystal structure shows that there are 6-fold robust hydrogen bonded interactions between $[Ru(H_2biim)_3]^{3+}$ cation and TMA anion. We suppose the robust hydrogen bonded interactions would be related to cooperative proton electron transfer. To address this hypothesis, complex $[Ru(H_2biim)_3](PF_6)_2$ was selected as a precursor to examine in detail the interaction with carboxylate via hydrogen bonding. In this contribution, we describe our first observation of the quantitative and rapid synthesis of a three-dimensional (3D) hydrogen bonding network $\{[Ru(H_2biim)_3](TMA)\} \cdot 5H_2O$ ($\mathbf{1 \cdot H_2O}$) via the "liquid-assisted"

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Table 1. Crystal Data and Structure Refinement for Complexes 1−3

complex	**1**	**2**	**3**
formula	$C_{27}H_{21}N_{12}$ O_6Ru	$C_{27}H_{21}N_{12}$ O_6Ru	$C_{27}H_{22}N_{12}$ O_6Ru
formula weight	710.63	710.63	711.63
crystal system	orthorhombic	orthorhombic	monoclinic
space group	*Fddd*	*Pbcn*	*P*2$_1$/*c*
a (Å)	10.7082(4)	16.9242(13)	9. 2410(12)
b (Å)	32.3079(9)	29.187(2)	12.4659(15)
c (Å)	58.660(2)	10.8676(9)	24.306(3)
b (deg)	90	90	96.541(2)
V (Å^3)	20294.0(2)	5368.2(7)	2781.8(6)
D_c (g cm^{-3})	0.930	0.879	1.699
Z	16	4	4
m (mm^{-1})	0.346	0.327	0.630
data/restraints/parameters	3324/0/210	3099/0/210	3522/0/415
GOF on F^2	1.01	1.02	1.01
R_1 [$I > 2\sigma(I)$], wR_2 (all data)^a	0.0504, 0.1238	0.0383, 0.0862	0.0619, 0.1776
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.56/−0.67	0.47/−0.37	0.80/−0.58

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

solid state reaction approach. The reaction occurs within minutes of grinding together [Ru(H$_2$biim)$_3$](PF$_6$)$_2$ and Na$_2$HTMA with a few drops of H$_2$O$_2$ as an oxidant and solvent, and the byproducts can then be simply removed by washing. The formation of the product is apparent by a color change from yellow to blue-green over the course of ca. 15 min. The single crystal large enough for X-ray diffraction analysis was obtained via seeding. To compare with the solid-state reaction, similar reactions were also carried out in an EtOH solution. Interestingly, two new complexes {[Ru(H$_2$biim)$_3$]-(TMA)}·10H$_2$O (**2·H$_2$O**) and [Ru(H$_2$biim)$_3$](HTMA) (**3**) were isolated in the presence of a polypyridine base, such as 2,2-dipyridylammine (dpa), 2,2′:6′,2″-terpyridine (tpy), or 1,10-phenanthroline (phen). Complexes **1** and **2** are topological isomers, in which **1** is a (10,3)-*b* 3D hydrogen-bonded network, whereas the latter is a (6,3) honeycomb two-dimensional (2D) hydrogen-bonded network.

Experimental Section

Materials and Methods. The reagents and solvents employed were commercially available and were used as received without further purification. The C, H, and N microanalyses were carried out with a Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 400−4000 cm^{-1} on a Bruker TENSOR 27 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Varian Mercury-Plus 300 NMR spectrometer with chemical shifts (in ppm) relative to tetramethylsilane (TMS). Powder X-ray diffraction patterns were recorded on a D8 ADVANCE diffractometer with Cu Kα radiation at a scanning rate of 4° min^{-1} with 2θ ranging from 4° to 40°. Thermogravimetric data were collected on a Netzsch TG-209 analyzer in nitrogen at a heating rate of 10 °C min^{-1}. The H$_2$biim[30] and [Ru(H$_2$biim)$_3$](PF$_6$)$_2$·3H$_2$O[31] were synthesized as the published procedures, respectively, and checked with elemental analysis and NMR spectra.

Solid-State Synthesis of {[Ru(H$_2$biim)$_3$](TMA)}·5H$_2$O (1·H$_2$O). A stoichiometric 1:1 mixture of [Ru(H$_2$biim)$_3$](PF$_6$)$_2$·3H$_2$O (0.1 mmol, 0.084 g) and Na$_2$HTMA (0.1 mmol, 0.025 g) was manually ground in an agate mortar for 15 min, and in this period four drops of 30% H$_2$O$_2$ (0.2 mL) were added to facilitate the reaction. The color of the material change from yellow to blue-green indicated that the reaction took place over the course of grinding. The product was washed by water (5 mL), then EtOH (5 mL) under reduced pressure to remove the byproduct NaPF$_6$. Finally, the product was dried in air at room temperature for 3 h. Yield, 99%. Single crystals of **1·H$_2$O** were obtained by the addition of the solid-state reaction product (polycrystalline) as seeds to a mixture of

Table 2. Selected Hydrogen Bonding Lengths (Å) and Bond Angles (°) of 1−3 (D, Donor Atom; A, Acceptor Atom)^a

D−H···A	D−H	H···A	D···A	∠D−H···A
		1		
N2−H2B···O2a	0.879(3)	1.782(2)	2.656(4)	174.0(2)
N4−H4A···O1a	0.881(3)	1.737(2)	2.617(4)	174.8(2)
N6−H6B···O3	0.882(3)	1.752(2)	2.630(4)	173.8(2)
		2		
N2−H2B···O2a	0.860(2)	1.772(2)	2.629(3)	173.1(2)
N4−H4A···O1a	0.860(2)	1.823(2)	2.666(3)	166.4(2)
N6−H6B···O3	0.861(2)	1.801(2)	2.647(3)	167.0(2)
		3		
O1−H1B···O2a	0.841(5)	1.824(5)	2.663(7)	174.8(4)
N2−H2B···O6b	0.860(5)	1.800(5)	2.636(7)	163.6(4)
N4−H4A···O4c	0.860(5)	1.949(4)	2.750(6)	154.5(4)
N6−H6B···O3d	0.860(5)	2.038(4)	2.806(6)	148.2(4)
N8−H8B···O3d	0.860(5)	2.214(4)	2.953(7)	143.9(4)
N10−H10A···O3	0.860(5)	1.958(4)	2.758(6)	154.3(3)
N12−H12B···O6e	0.859(5)	2.048(5)	2.759(7)	139.5(4)

^{a} Symmetry code, **1**, a: 1/2 − *x*, −1/4 + *y*, 1/4 + *z*; **2**, a: 1/2 − *x*, −1/2 + *y*, −*z*; **3**, a: −*x*, 1 − *y*, 1 − *z*; b: 1 + *x*, 3/2 − *y*, −*y* + *z*; c: 1 − *x*, −1/2 + *y*, 1/2 − *z*; d: 1 − *x*, 1/2 + *y*, 1/2 − *z*; e: −*x*, 2 − *y*, 1 − *z*.

[Ru(H$_2$biim)$_3$](PF$_6$)$_2$·3H$_2$O and H$_3$TMA (1: 1) in an EtOH solution at room temperature in 1 week. C$_{27}$H$_{31}$N$_{12}$O$_{11}$Ru$_2$ (800.61): C 40.47, H 3.87, N 20.98; found C 40.39, H 3.72, N 20.42. FT-IR data (cm^{-1}): 3500−2800 br, 1638 m, 1551 s, 1359 vs, 1185 m, 1130 m, 1095 m, 1001 m, 922 m, 758 m, 709 m, 526 m. The TGA experiment of **1·H$_2$O** was carried out from 20 to 450 °C. The weight loss of 11.3% in the range of 20−200 °C (see Figure S1 in the Supporting Information) corresponds to the loss of five water molecules (calculated 11.2%).

Syntheses of {[Ru(H$_2$biim)$_3$](TMA)}·10H$_2$O (2·H$_2$O) and [Ru(H$_2$biim)$_3$](HTMA)} (3). H$_3$TMA (0.05 mmol, 0.011 g) and phen (0.15 mmol) were added to the solution of [Ru(H$_2$bbim)$_3$](PF$_6$)$_2$·3H$_2$O (0.05 mmol, 0.042 g) in an EtOH (20 mL). The mixture solution was stirred at room temperature for 10 min and filtered. The filtrate was kept at room temperature to volatilize the solvent. After one week, the yellow crystals of **3** were collected. Yield, 40%. The blue-green **2·H$_2$O** crystallized from the mother solution in 1 month. Yield, 20%. C$_{27}$H$_{41}$N$_{12}$O$_{16}$Ru (**2·H$_2$O**, 890.63): C 36.38, H 4.60, N 18.86; found C 35.92, H 4.22, N 18.46. FT-IR data (cm^{-1}) for **2·H$_2$O**: 3510−2700 br, 1635 m, 1552 s, 1355 vs, 1183 m, 1128 m, 1092 m, 1000 m, 920 m, 755 m, 706 m, 524 m. The TGA experiment of **2·H$_2$O** was carried out from 20 to 600 °C. The weight loss of 20.6% in the range of 20−210 °C (see Figure S2 in the Supporting Information) corresponds to the loss of 10 water molecules (calculated 20.2%). C$_{27}$H$_{22}$N$_{12}$O$_6$Ru (**3**, 711.64): C 45.53, H 3.09, N 23.61; found C 45.47, H 3.12, N 23.52. FT-IR data (cm^{-1}) for **3**: 3257−2519 br, 1690 s, 1616 s, 1573 s, 1351 s, 1186 m, 1103 m, 934 s, 746 s, 690 s.

X-ray Crystallography. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table 1. Selected hydrogen bonds are listed in Table 2. Diffraction intensities were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using SADABS.[32] The structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELXS-97 and SHELXL-97 programs, respectively.[33] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C−H 0.96 Å and N−H 0.86 Å). The solvent molecules in **1** and **2** were highly disordered at this temperature. Efforts to locate and refine the solvent peaks were in vain. The SQUEEZE routine was used to remove the scattering from the highly disordered solvent molecules. The structures of **1** and **2** were then refined again using the new intensity data generated by SQUEEZE.[34] Statistics prior to treatment of data with SQUEEZE were R_1 = 0.0810, 0.0713 ($I > 2\sigma(I)$), wR_2 = 0.2646, 0.2500 (all data), and S = 1.02, 1.01, for **1** and **2**, respectively.

(a)   (b)

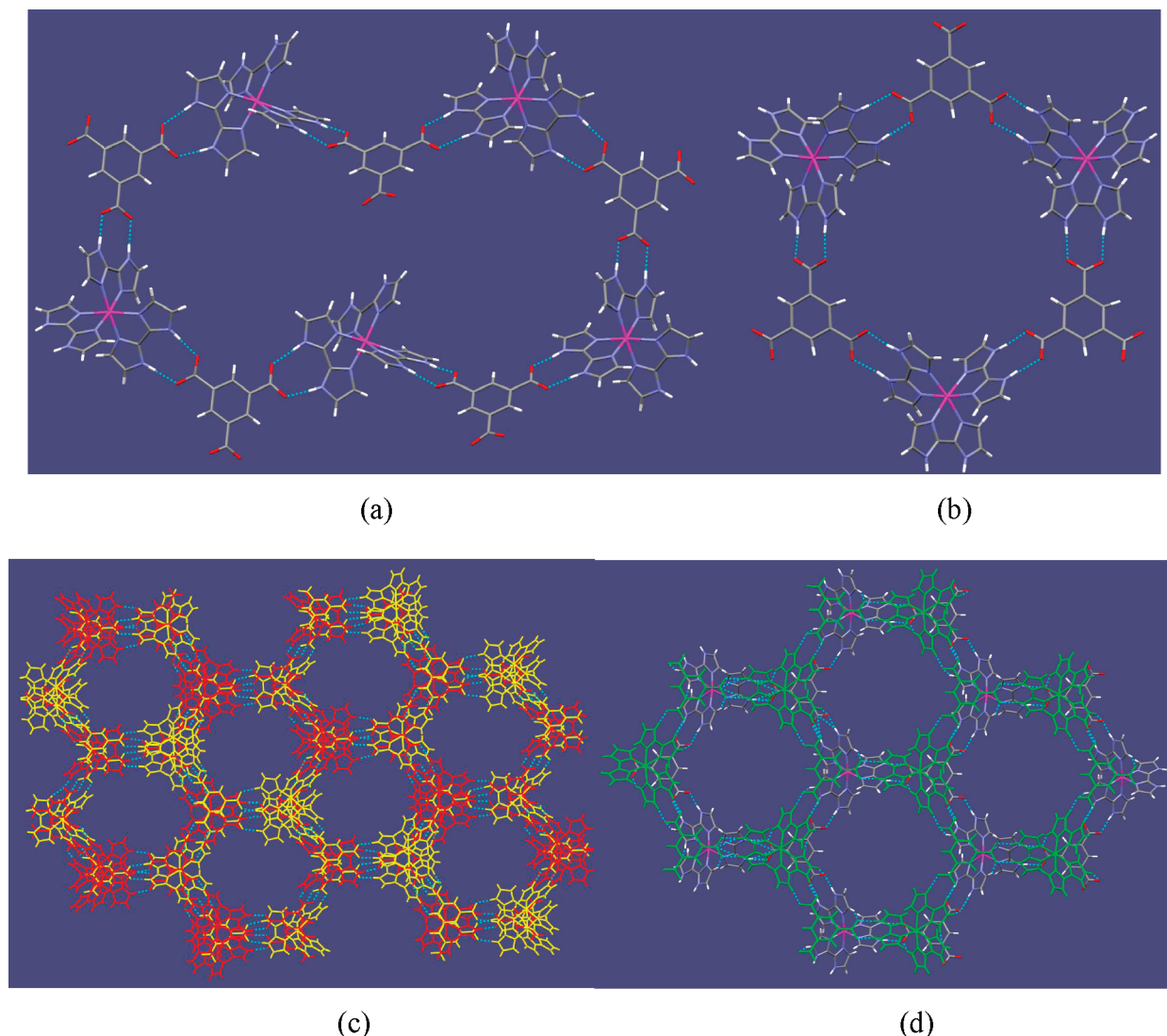(c)   (d)

Figure 1. Views of (a) a (10,3)-*b* unit and (c) the 2-fold interpenetrating 3D (10,3)-*b* nets in **1**; (b) a (6,3) unit and (d) the double layers of the 2D (6,3) nets in **2**.

Results and Discussion

Crystal Structures 1 and 2. Although chemical component of complexes **1** and **2** are almost the same, they crystallize in centrosymmetric space groups *Fddd* and *Pbcn*, respectively, with different unit cell parameters (see Table 1). Each Ru(III) ion is coordinated by six nitrogen atoms from three H_2biim ligands, resulting in a distorted octahedral structure. More-over, each $[Ru(H_2biim)_3]^{3+}$ cation links to three TMA anions via three pairs of strong hydrogen bonds [N2···O2a = 2.656(4), N4···O1a = 2.617(4), and N6···O3 = 2.630(4) Å for **1** and N2···O2a = 2.629(3), N4···O1a = 2.666(3), and N6···O3 = 2.647(3) Å for **2**] with $R^2_2(9)$ synthons into a 3D (10,3)-*b* net for **1** and a 2D (6,3) net for **2** (Figure 1a,b). This complementary, charge-assisted hydrogen bonding is so robust that it is widely employed in crystal engineering.[22−26] Alternately, each TMA anion connects to three $[Ru(H_2biim)_3]^{3+}$ cations via hydrogen bonds. Therefore, they are topological isomers. In **1**, two sets of the (10,3)-*b* nets wrap each other generating a 2-fold interpenetration 3D hydrogen bonded network with 1D channels (Figure 1c). The channel diameter, obtained by subtracting the van der Waals radius of the hydrogen atoms, is estimated to be

approximately 11 Å. Analysis of the crystal volume available for the solvents by using PLATON shows that there is approximately 50% after removal of the lattice water mole-cules. In **2**, the 2D (6,3) layers stack in face-to-face producing 1D channels with an approximately 17 Å diameter (Figure 1d) and 52% volume available for solvent entrance. These values are larger than those in **1**, indicating that the space occupancy in the (10,3)-*b* isomer is higher than that in the (6,3) one. However, the positions of the solvent molecules cannot be accurately ascertained due to the disorder of the water molecules at room temperature. The numbers of the water molecule were confirmed by thermal gravimetric analysis (TGA).

Crystal Structure of 3. To compare the structural para-meters between $[Ru(H_2biim)_3]^{2+}$ and $[Ru(H_2biim)_3]^{3+}$, the Ru(II) species **3** was synthesized and measured by X-ray single crystal determination. It consists of one $[Ru(H_2biim)_3]^{2+}$ cation and one $HTMA^{2−}$ anion. As ex-pected, Ru(II) ion is coordinated by three H_2biim ligands in a distorted octahedral coordination. The distances of Ru-(II)−N (2.058(5)−2.080(5) Å) are also comparable to those observed in **1** and **2** (Ru(III)−N (2.045(3)−2.071(3) Å for **1** and 2.049(2)−2.063(2) Å for **2**). The bite angles of N−Ru−N
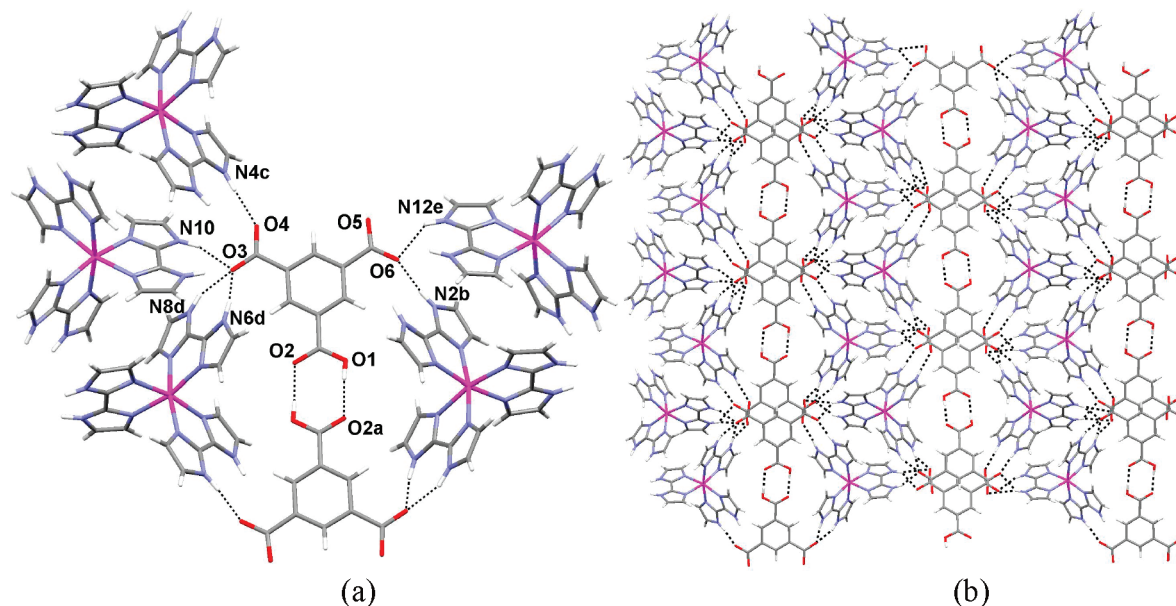
Figure 2. Views of (a) the hydrogen bonded connection and (b) 2D hydrogen bonded network in **3**. Symmetry code: a, $-x, 1 - y, 1 - z$; b, $1 + x$, $3/2 - y, -y + z$; c, $1 - x, -1/2 + y, 1/2 - z$; d, $1 - x, 1/2 + y, 1/2 - z$; e, $-x, 2 - y, 1 - z$.
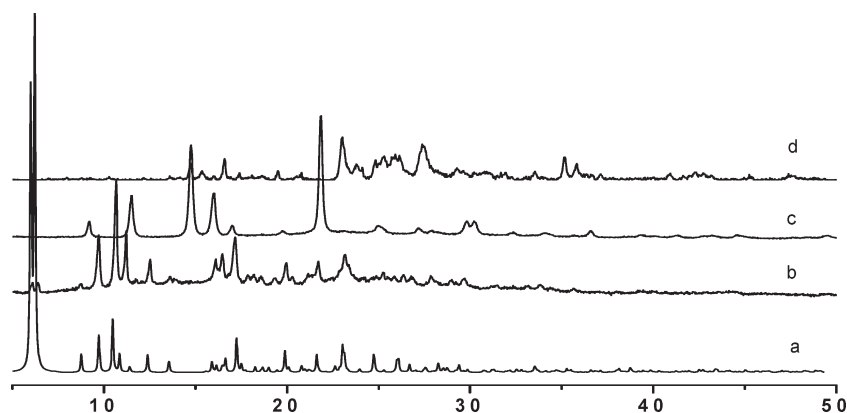

Figure 3. Powder XRD patterns of (a) the simulation based on the single-crystal analysis of **1**, (b) as-synthesized sample by grinding, (c) $[Ru(H_2biim)_3](PF_6)_2$, and (d) Na_2HTMA.

are $78.1(2)-78.3(2)°$ are slightly smaller than those observed in **1** $(79.3(2)-79.4(2)°)$ and **2** $(78.9(8)-79.2(8)°)$, indicating no significant structural changes in the primary coordination sphere between $[Ru(H_2biim)_3]^{2+}$ and $[Ru(H_2biim)_3]^{3+}$, though the complex color changes from orange yellow to blue green. However, the geometries and the hydrogen bonded models of the carboxylate are much different. As shown in Figure 2a, the O1 atom is protonated and strong hydrogen bonding to the O2a atom from the neighboring HTMA $(O1\cdots O2a = 2.663(7)$ Å), resulting in a dimer model. The dimer $[HTMA-HTMA]^{4-}$ unit further connects to $[Ru(H_2biim)_3]^{2+}$ cations via $N\cdots O$ hydrogen bonds into a 2D network (Figure 2b). Marked differences from **1** and **2**, the O6 atom in compound **3** is diplex hydrogen bonded to N2b $(N2b\cdots O6 = 2.636(7)$ Å) and N12e $(N12e\cdots O6 = 2.759(7)$ Å), and the O3 atom is triplex hydrogen bonded to N6d $(N6d\cdots O3 = 2.806(6)$ Å), N8d $(N8d\cdots O3 = 2.953(7)$ Å) and N10 $(N10\cdots O3 = 2.758(6)$ Å) from two $[Ru(H_2biim)_3]^{2+}$ cations, resulting in bond lengths of C26−O6 $(1.252(9)$ Å) and C23−O4 $(1.257(6)$ Å) longer than those of C26−O5 $(1.228(8)$ Å) and C23−O3 $(1.242(8)$ Å). For each $[Ru(H_2biim)_3]^{2+/3+}$ cation, the number of hydrogen

bonding is the same, however, the fashion and the strength are much different. In complexes **1** and **2**, the hydrogen bonding is very strong $(N\cdots O = 2.63$ and 2.64 Å) in a $R^2_2(9)$ synthon, while in compound **3**, the average $N\cdots O$ distance is 2.78 Å. The robust hydrogen bonding in complexes **1** and **2** may trigger the proton transfer, then electron transfer, such as the description by Steiner: "all hydrogen bonding can be considered as incipient proton-transfer reactions, and for strong hydrogen bonding, this reaction can be in a very advanced state".[35]

Solvent-Assisted Solid-State Reaction. Recently, we primarily reported the structure of the complex {[Ru-$(H_2biim)_3](TMA)$}·DMF·9H_2O that was obtained during the complexation of $[Ru(H_2biim)_3](PF_6)_2$ and H_3TMA from solution.[29] In this course, the stable species $[Ru(H_2biim)_3]^{2+}$ (yellow) was oxidized to $[Ru(H_2biim)_3]^{3+}$ (blue-green) in the air-exposed solution. We suspect the robust hydrogen bonded interactions between the $[Ru(H_2biim)_3]^{3+}$ cation and TMA anion would be related to cooperative proton electron transfer, resulting in a Ru(III) status. On the other hand, the cocrystals of hydrogen-bonded system were widely prepared by grinding the solid components together.[4] Keeping these in

Scheme 1. Schematic Representation of the Syntheses of 1−3 from Solution and Solid-State Reaction
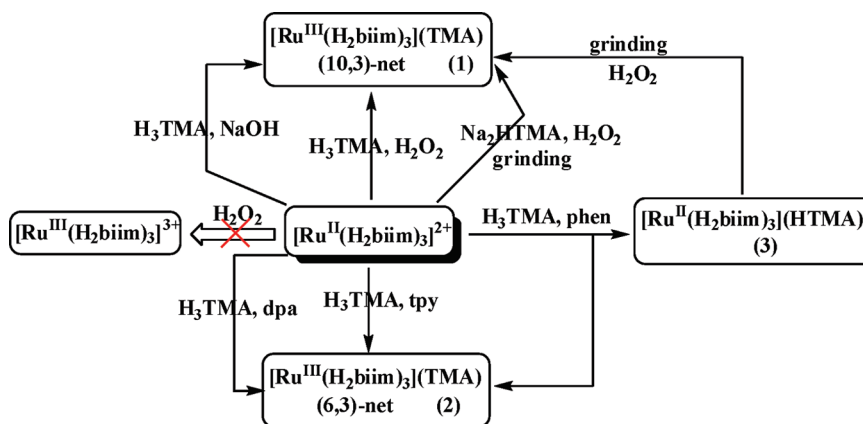
mind, the mechanochemical approach was applied to assemble the $[Ru(H_2biim)_3]^{2+}$ and H_3TMA. The complex **1** could be quantitatively and rapidly obtained as a polycrystalline sample by manual grinding of the solid $[Ru(H_2biim)_3]^{2+}$ and Na_2HTMA reactants in a 1:1 ratio. In this period, a few drops of H_2O_2 were added to increase the reaction. The formation of complex **1** was indicated by a change in color from the original yellow (Ru(II) color) to final blue-green (Ru(III) color). Powder X-ray diffraction showed the product to be highly crystalline, and also revealed that the reaction was quantitative, since no starting materials were detected, as shown in Figure 3. Although quinhydrone charge-transfer complexes had been reported upon solid-state grinding,[12] the observation of redox reaction for coordination compound by the grinding is relatively rare.[2] To examine the effect of hydrogen bonding in the redox reaction, two control experiments were carried out. First, when a few drops H_2O_2 were added to the solid $[Ru(H_2biim)_3]$-$(PF_6)_2$, then grinding, no color change was observed. Powder X-ray diffraction showed that no new species formed. Second, a few drops of solvent such as H_2O or methanol was added to the mixture of $[Ru(H_2biim)_3](PF_6)_2$ and Na_2HT-MA, then grinding, and the redox reaction also took place, but very slowly. The color changed to blue-green after the reaction was exposed in air for several days. The above experiments indicate that H_3TMA is necessary for the redox reaction. We know that the distal deprotonation of imidazole can reduce the redox potential of metal center.[13−17] The more deprotonation of H_2biim ligands makes the redox potentials of Ru(II) complex shift to a less positive value. Crystal structure of **1** shows that there are 6-fold robust hydrogen bonded interactions between one $[Ru(H_2biim)_3]^{3+}$ cation and three TMA anions. Such strong interaction may trigger the proton transfer from H_2biim to TMA,[35] which greatly increases the electron density at the Ru(II) center, and finally shifts its oxidation potential to a less positive value.[28]

To obtain single crystal of **1**, the polycrystalline sample obtained from grinding was then added to the mixture solution of $[Ru(H_2biim)_3](PF_6)_2$ and H_3TMA as seeds. Single crystals of **1** suitable for X-ray diffraction were obtained in a few days. Its stimulated PXRD pattern based on the crystal structure analysis allowed unambiguous identification of the solid-state reaction products via a comparison of the experimental and computed powder diffraction patterns (Figure 3). A good fit was obtained for the positions of the main reflections, but discrepancies in the intensities remain. These discrepancies might result from preferred crystallite orientation and anisotropic particle broadening.

In our instance, the same structure was obtained from both the solid-state reaction and solution via seeds. However, in some cases, the reaction products obtained from different approaches are different.[36] Therefore, diverse methods were applied to examine the reaction and summarized in Scheme 1. When 2 equiv of NaOH or H_2O_2 was respectively added to the mixture solution of $[Ru(H_2biim)_3]$-$(PF_6)_2$ and H_3TMA, complex **1** was also obtained. Interestingly, complex **2** was obtained in the presence of a weak base such as dpa or tpy. Complex **2** is a (6,3) honeycomb 2D hydrogen-bonded network and topological isomer to complex **1**. However, which factors may affect and mediate the structure and how to control the structure still remain a great challenge.[37] Surprisingly, when phen was added to the above solution, complex **3** crystallized in yellow from the solution first. By keeping the mother solution in evaporation, complex **2** crystallized in blue-green in a month. In complex **3**, the Ru(II) ion is not oxidized to Ru(III) ion, and one of carboxylate groups of TMA is protonated, which can be seen as an intermediate in the course complexation. To address this hypothesis, the solid **3** was used as a starting material and grinded with a few drops of H_2O_2, and the color changed from yellow to blue-green in several minutes. Powder XRD pattern showed that complex **1** was also obtained via grinding of the solid complex **3**. The above experiments suggest that solution crystallization may at times offer more product diversity than grinding.

Conclusion

In summary, the grinding together of $[Ru(H_2biim)_3](PF_6)_2$ ion and Na_2HTMA is demonstrated as a convenient and effective preparative method for a robust, 3D hydrogen bonded network. The mechanochemical reactions imply a profound solid-state rearrangement accompanied by breaking and forming of hydrogen-bonding interactions. On the other hand, the multiple robust hydrogen bonds between the $[Ru(H_2biim)_3]^{3+}$ and TMA may trigger the proton transfer from H_2biim to TMA, which then shifts the Ru(II) oxidation potential to a less positive value. This subtle method of modification potentially allows for a greater control of the stability of transition metal complexes while avoiding the need for complicated synthetic manipulations.

Supporting Information Available: TG for **1** and **2**; X-ray crystallographic files in CIF format for the structure determination of **1**−**3**. This information is available free of charge via the Internet at http://pubs.acs.org.

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