

Cite this: *CrystEngComm*, 2011, **13**, 4512

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PAPER

Liquid-assisted solid-state reaction: assembly of (6,3) and (10,3) hydrogen-bonded networks based on $[M(\text{Hbiim})_3]$ by oxidation of $[M(\text{H}_2\text{biim})_3]^{2+}$ complexes in the presence of acetate anions†

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Received 5th January 2011, Accepted 23rd February 2011

DOI: 10.1039/c1ce00009h

Two complexes $[\text{Ru}(\text{Hbiim})_3]$ (**1**) and $[\text{Co}(\text{Hbiim})_3] \cdot 3\text{H}_2\text{O}$ (**2**) (H_2biim = 2,2'-biimidazole) were synthesized quantitatively and rapidly *via* a “liquid-assisted” solid-state reaction approach. The reaction occurs within minutes of grinding together $[\text{Ru}(\text{H}_2\text{biim})_3](\text{PF}_6)_2$ or $[\text{Co}(\text{H}_2\text{biim})_3]\text{Cl}_2$ and NH_4OAc with a few drops of H_2O_2 as an oxidant and solvent, concomitant with colour changes. The structures of the compounds obtained from the solid-state reaction were confirmed by comparison of their PXRD patterns with simulations based on their single crystal structures. Complex **1** is a 3-fold interpenetrating three-dimensional hydrogen bonded polycatenate network based on a (6,3) net, complex **2** is a double-layer network linked by the lattice water molecules and the Hbiim ligands *via* hydrogen bonds. For comparison with the solid-state reaction, control reactions were also carried out in solution. Complex **1** was also afforded from the solution reaction. However, a new phase $[\text{Co}(\text{Hbiim})_3] \cdot 0.5\text{EtOH}$ (**3**) was obtained from solution, rather than **2**, although it also crystallized from an identical solution of EtOH–water. Complex **3** is a 4-fold interpenetrating three-dimensional hydrogen bonded polycatenate network based on a (10,3)-b net. Interesting, the $[\text{M}(\text{H}_2\text{biim})_3]^{2+}$ (M = Ru and Co) species can be oxidized to the corresponding $[\text{M}(\text{Hbiim})_3]$ species by oxygen in the presence of acetate anions, which play a determined role in the redox reaction. The deprotonation of the $[\text{M}(\text{H}_2\text{biim})_3]^{2+}$ species triggered by the acetate anions greatly increases the electron density at the M(II) center and shifts the oxidation potentials of M(II) complex to a less positive value. This may provide an effective approach for the generation of high status metal complexes *via* supramolecular interactions.

Introduction

Solid-state reactions have been widely applied in organic reactions,¹ especially photochemical reactions,² since the pioneering work of Etter and co-workers.³ An efficient approach for solid-state reactions is to mill or grind the solid reactants together. These methods have also been successfully applied in the field of molecular crystal engineering for the solvent free preparation of supramolecular aggregates, co-crystals and metal–organic frameworks.^{4–6} The scope of solid-state synthesis in coordination chemistry has been established but remains relatively under-exploited. Moreover, there is some evidence to indicate that the

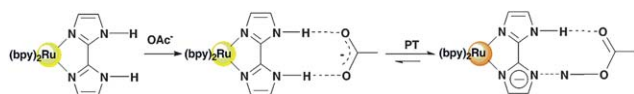
addition of minor amounts of a particular solvent to the grinding process, termed “solvent-assisted” mechanochemistry, can result in a dramatic increase in the yield, reaction rate and product crystallization in solid-state synthesis.^{7–9}

Recently, we and others have exploited the strategy of second-sphere coordination to design ionic receptors based on 2,2'-biimidazole-like (H_2biim) complexes in solution.^{10–14} The most interesting and important feature for such complexes is that the chelating coordination of the H_2biim ligand enforces the *syn* conformation and engages in robust hydrogen bonding *via* the externally directed pair of N–H groups to a carboxylate group.^{15–19} Furthermore, the strong electron-withdrawing effect of metal center greatly enhances the acidity of the N–H groups.^{20,21} This is indeed the case for the $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{biim})](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine) complex; the formation of dual robust hydrogen bonds between the H_2biim ligand and the OAc^- anion triggers a proton transfer from H_2biim to the carboxylate group, resulting in monodeprotonation of H_2biim ligand, and a color change in the complex from yellow to orange–brown because of the second sphere donor–acceptor interactions between Ru(II)– H_2biim and the OAc^- anion (see Scheme 1).¹⁰ Such interactions greatly increase the electron density of the Ru(II) center and shift

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† Electronic supplementary information (ESI) available: TG for **2**; photographs of the solid-state reaction for complexes **1** and **2**; CV curves of $[\text{Ru}(\text{H}_2\text{biim})_3](\text{PF}_6)_2$ in acetonitrile upon addition of Bu_4NOAc . CCDC reference numbers 806449–806451. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ce00009h



Scheme 1 A schematic representation of the proton transfer from H₂biim to an OAc[−] anion.

its oxidation potential to a less positive value.²² It was proved that the increased deprotonation at remote sites of imidazole ligands resulted in a shift in the redox potentials of a metal center to much less positive values.^{23–26} This may afford an effective approach for the preparation of high status metal complexes *via* modification of the potential. On the other hand, the complex {[Ru(H₂biim)₃](TMA)}·DMF·9H₂O (H₃TMA = trimesic acid) which has a three dimensional network was obtained serendipitously during the complexation of [Ru(H₂biim)₃](PF₆)₂ and H₃TMA in a solution of DMF–EtOH at room temperature.²⁷ We found that the original stable species [Ru(H₂biim)₃]²⁺ (d⁶ electron state) was oxidized to [Ru(H₂biim)₃]³⁺ (d⁵ electron state) in the air-exposed solution. Careful examination of its crystal structure shows that there are 6-fold robust hydrogen bonded interactions between each [Ru(H₂biim)₃]³⁺ cation and three TMA anions. This is reminiscent of the robust hydrogen bonded interactions which induced proton and electron transfer.²⁸ We have also expanded this reaction to solid-state synthesis and successfully synthesized a two dimensional hydrogen bonding network {[Ru(H₂biim)₃](TMA)}·5H₂O quantitatively.²⁹ However, its molecular structure is different from the one obtained from solution complexation; they are topological isomers. Although charge-transfer complexes have been reported in solid-state grinding over a century ago,³⁰ the observation of a redox reaction to form coordination compounds by solid-state synthesis is relatively rare.^{29,31} As part of an ongoing study, we observe here an oxidation reaction of [Ru(H₂biim)₃]²⁺ to [Ru(Hbiim)₃] by a “liquid assisted” solid-state reaction in the presence of acetate anions. Their colours change from yellow to blue over the course of grinding. The unique complex [Ru(Hbiim)₃] (**1**) was afforded both from the solution and solid-state reactions. We also extended the reaction to the synthesis of a [Co(Hbiim)₃] complex. However, we found that two phases [Co(Hbiim)₃]·3H₂O (**2**) and [Co(Hbiim)₃]·0.5EtOH (**3**) were obtained from solid-state and solution reactions, respectively.

Results and discussion

Crystal structure of **1**

Complex **1** crystallizes in a space group *P2₁/c*, with different unit cell parameters from the previous report of {[Ru(Hbiim)₃]}₂.³² As shown in Fig. 1a, each Ru(III) ion is coordinated by six nitrogen atoms from three Hbiim ligands [Ru(1)–N = 2.033(3)–2.092(3) Å], resulting in a distorted octahedral structure. The main distortion of the resulting octahedral coordination geometry originates from the small bite angle of the chelating H₂biim ligand (77.7(1)–79.0(1)°). The geometry of the [Ru(Hbiim)₃] molecule is comparable to the previously reported values in {[Ru(Hbiim)₃]}₂ (2.064(4) Å and 78.5(2)°),³² [Ru(H₂biim)₃]²⁺ (2.047(5)–2.085(5) Å and 76.9(3)–78.8(2)°),³³ and [Ru(H₂biim)₃](TMA) (2.045(3)–2.071(3) Å and (78.9(8)–79.4(8)°),^{27,29}

indicating no significant structural changes in the primary coordination sphere between [Ru(H₂biim)₃]²⁺, [Ru(Hbiim)₃], and [Ru(H₂biim)₃]³⁺, although the colour of the complexes change from orange–yellow to blue. As shown in Fig. 1b, the neutral Δ- and Λ-[Ru(Hbiim)₃] molecules alternately connect to each other *via* complementary intermolecular N–H⋯N hydrogen bonds (2.744(9)–2.766(9) Å) with *R*²₂(10) synthons. This alternating sequence of Δ and Λ isomers allows the hydrogen bonded *R*²₂(10) synthons formed by a given molecule to reside roughly in the same plane with its three neighbours, generating six-membered rings that propagate into a two-dimensional honeycomb (6,3) network. The (6,3) sheets are alternately stacked in a offset fashion (see Fig. 1c), and the interlayer distance is *ca.* 6.8 Å. Moreover, three sets of the (6,3) nets wrap each other compactly generating a solvent-free 3-fold interpenetrating three dimensional hydrogen bonded polycatenate network (see Fig. 1d). Although two isomers of the analogous species of racemic [Co(Hbiim)₃] with (6,3) and (10,3)-b nets were obtained from different solvents,^{34,35} in our case, only a (6,3) honeycomb sheet was obtained from both solution and solid-state reactions (*vide infra*). It should be noted that the structure of complex **1** is very different from that of [Co(Hbiim)₃]·CH₃CO₂Et·CH₃OH with a (6,3) net, in which the (6,3) sheets are arranged parallel with channels that are filled with the solvent molecules.³⁴

Crystal structures of **2** and **3**

To compare the different phases obtained from solution and solid-state reactions, their structures were measured by X-ray single crystal determination. They all consist of a neutral [Co(Hbiim)₃] molecule and solvent molecules, however, their structures are significantly different, although their single crystals were grown from an identical solution of EtOH–H₂O. Complex **2** with three water molecules crystallizes in the space group *P2₁/n*, with different unit cell parameters from the report of [Co(Hbiim)₃] complexes.^{34,35} Complex **3** with half of an EtOH solvent molecule is in the *Pbcn* space group, with the same cell parameters as the [Co(Hbiim)₃]·0.5DMF·0.8H₂O complex,³⁵ indicating that they are isomorphous forms that differ essentially in solvate molecules. As expected, the Co(III) ion is coordinated by three Hbiim ligands in a distorted octahedral coordination as shown in Fig. 2a. The distances of Co(III)–N (1.911(4)–1.927(4) Å for **2** and 1.900(3)–1.940(3) Å for **3**) are also comparable to those observed in [Co(Hbiim)₃]·CH₃CO₂Et·CH₃OH (1.919(3)–1.956(3) Å),³⁴ [Co(Hbiim)₃]·0.5DMF·0.8H₂O (1.907(4)–1.939(4) Å),³⁵ and [Co(H₂biim)₃](NO₃)₃ (1.922(2) Å),³⁵ indicating no significant structural changes between [Co(Hbiim)₃] and [Co(H₂biim)₃]³⁺ (where the H₂biim ligand is neutral or mon-deprotonated). However, they are significant shorter than those observed in [Co(H₂biim)₃]²⁺ (2.138(3)–2.168(3) Å).³⁶ By careful examination of their structures, we find that the basic structural unit in complex **3** is a (10,3)-b net connecting the [Co(Hbiim)₃] molecules to each other *via* complementary N–H⋯N hydrogen bonds (2.761(7)–2.853(7) Å) with *R*²₂(10) synthons (see Fig. 2b). Moreover, the (10,3)-b nets wrap around each other generating a 4-fold interpenetrating three dimensional hydrogen bonded polycatenate network, similar to that observed in [Co(Hbiim)₃]·0.5DMF·0.8H₂O.³⁵ However, its structure is greatly different from [Co(Hbiim)₃]·CH₃CO₂Et·CH₃OH with a (6,3)

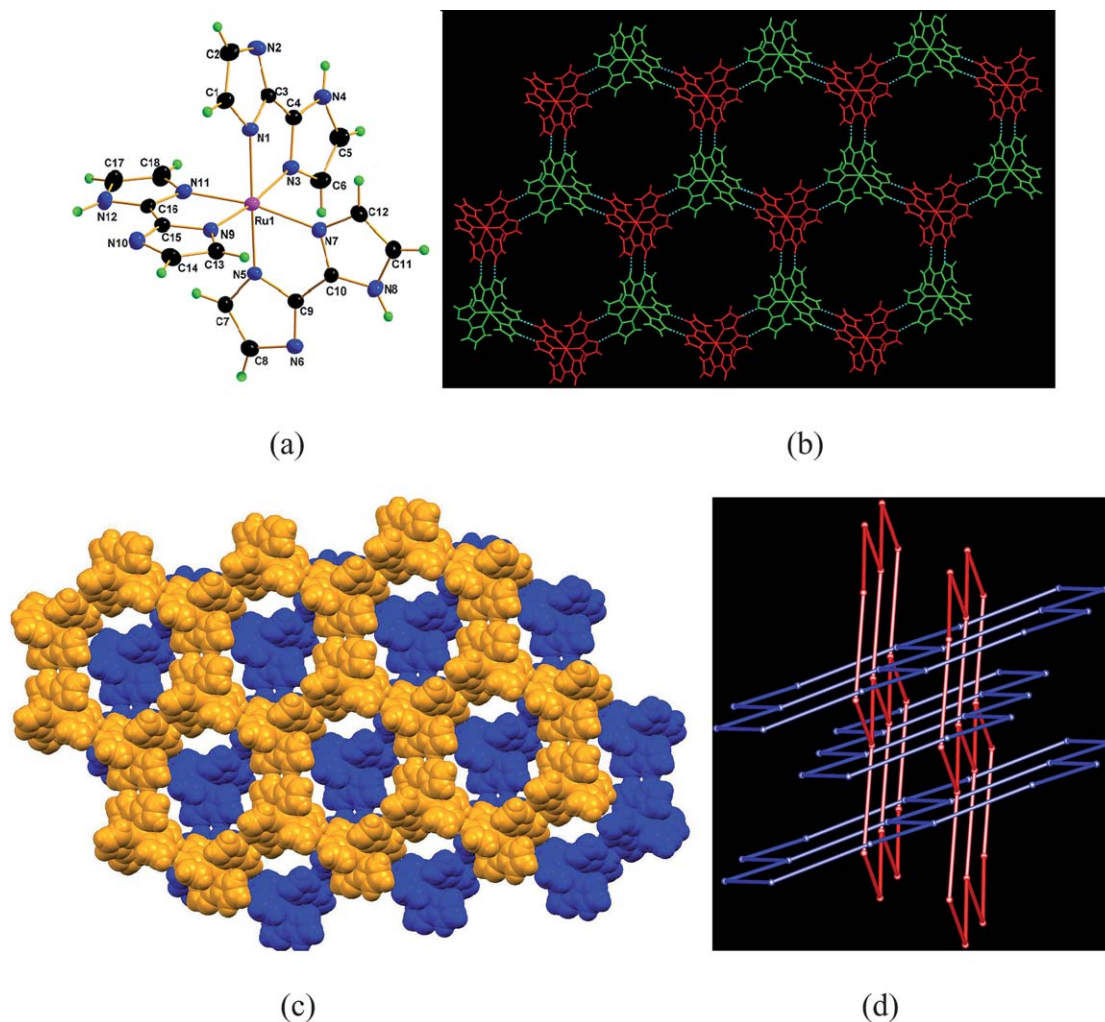


Fig. 1 Views of (a) the coordination environment of the Ru(III) ion, (b) a honeycomb 2D hydrogen-bonded sheet linked alternately by Δ (red) and Λ (green) isomers, (c) the CPK drawing of two layers in offset motif, and (d) the 3-fold interpenetrating of the polycatenate network in **1**.

net,³⁴ indicating that the solvent molecules play a determining role in the supramolecular assembly. In these cases, the networks all connect *via* complementary N–H...N hydrogen bonds with $R^2_2(10)$ synthons and the solvent molecules do not participate in hydrogen bonding with the [Co(Hbiim)₃] molecule. It is unclear why the change of solvents, from MeOH–CH₃CO₂Et to H₂O–DMF or EtOH, causes such a major change in the structure. A similar case was also reported by Tadokoro's group, in which the assembly of a [Ni(Hbiim)₃][–] unit into the (6,3) or (10,3) net depends greatly on the counterions present.³⁷

However, some differences were observed in complex **2**. As shown in Fig. 2a, water molecules form hydrogen bonds each other (O2W...O3W = 2.685(7), O1WA...O3WC = 3.070(7), and O2WB...O1W = 2.820(7) Å), and further donate and accept hydrogen bonds to the Hbiim ligands (N12...O1W = 2.812(7), N2...O2W = 2.916(7), N4...O3W = 2.761(7), N8...O1WA = 2.768(7), N10...O2WB = 2.758(7), and N6...O3WC = 2.863(7), Å), generating $R^3_3(9)$ synthons. Furthermore, the water molecules link to each other *via* hydrogen bonds, generating water chains along the *c* axis. These chains further connect with the [Co(Hbiim)₃] molecules to form a two dimensional hydrogen bonded network as shown in Fig. 2c. Within this sheet, the O1W

water molecule is in a tetrahedral geometry with two hydrogen bonded donors and two acceptors. While the O2W and O3W molecules involve three hydrogen bonds, which further donate (O3W) and accept (O2W) hydrogen bonds from the Hbiim ligands of other sheet, generating a double-layer network as shown in Fig. 2d. Although complexes **2** and **3** were prepared by different approaches, they consist of [Co(Hbiim)₃] and different solvent molecules. The solvent molecules may play a pivotal role in the molecule packing.³⁸ The lattice water molecule is a good hydrogen bonding partner, it participates as a hydrogen bond donor and acceptor to the Hbiim ligand without imposing strict directional constraints, and this leads to a different packing pattern.

Solid-state synthesis of **1**

Our primary study showed that the complex [Ru(H₂biim)₃]²⁺ can be oxidized to [Ru(H₂biim)₃](TMA) during the complexation of [Ru(H₂biim)₃](PF₆)₂ and H₃TMA, exposed to air, both from solution and solid-state grinding.^{27,29} We suppose that the robust, multiple hydrogen bonding interactions between the [Ru(H₂biim)₃]³⁺ cation and TMA anion would be related to the

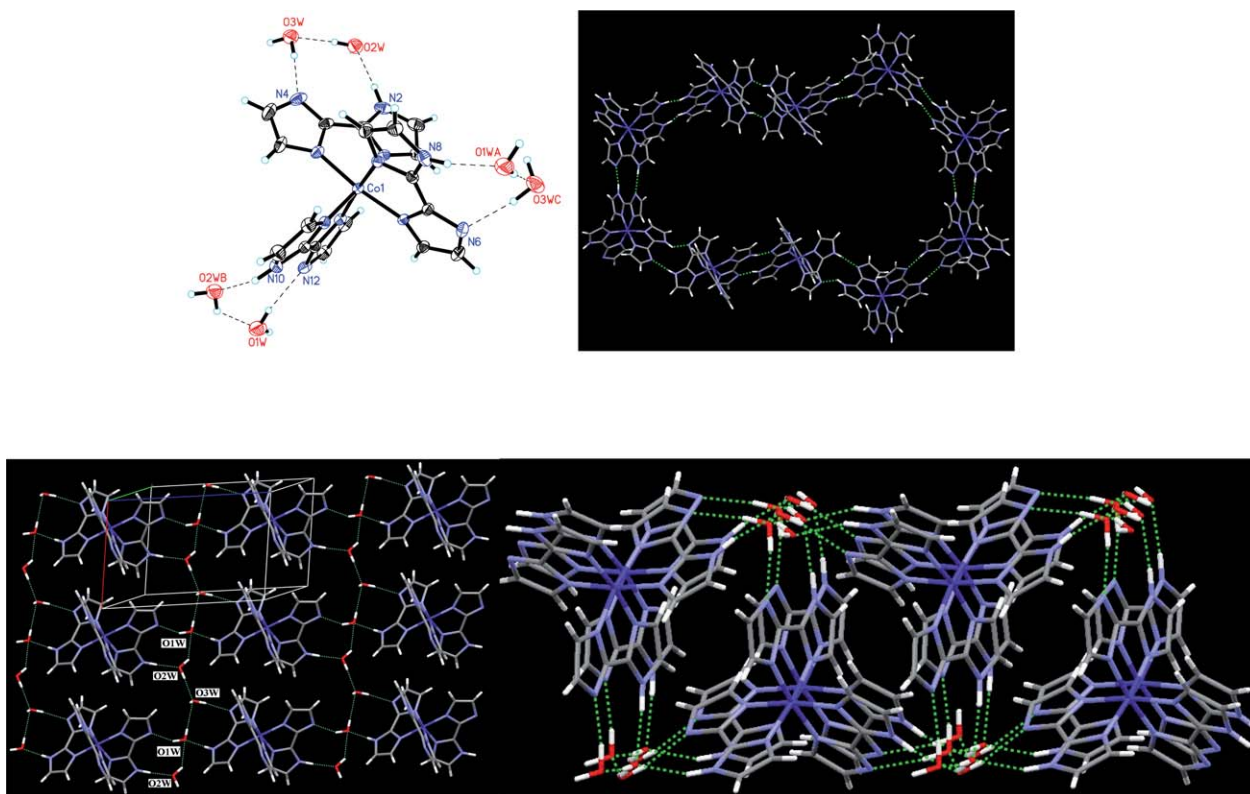


Fig. 2 Views of (a) the coordination environment of the Co(III) ion containing hydrogen bonds with water molecules in **2**, (b) the (10,3)-b hydrogen bonded network in **3**, (c) the two dimensional net linking through the water chain on the *ac* plane, and (d) the double-layers linked *via* hydrogen bonds along the *a* axis in **2**. Symmetry code: A, $-x, y, z - 1$; B, $x + 1/2, -y + 1/2, z + 1/2$; C, $x - 1/2, -y + 1/2, z - 1/2$.

cooperative proton electron transfer, resulting in a Ru(III) oxidation state. Here, the TMA anion is a conjugate base, accepting a proton from the $[\text{Ru}(\text{H}_2\text{biim})_3]$ cation. In a continuation of our interest in solid-state redox reactions in the presence of an anion, we extended the reaction to $[\text{Ru}(\text{H}_2\text{biim})_3](\text{PF}_6)_2$ and NH_4OAc , in which the acetate can be regarded as a weak base and triggers proton transfer from the H_2biim ligand to the acetate *via* the formation of hydrogen bonds.²⁸ Indeed, complex **1** was quantitatively and rapidly obtained as a polycrystalline sample by manual grinding of the solid $[\text{Ru}(\text{H}_2\text{biim})_3]^{2+}$ and NH_4OAc reactants in a 1 : 3 ratio. During this period, a few drops of H_2O_2 were added to the mixture of solid-state reactants to increase the reaction rate. The color changed from yellow to green, then to blue (see Fig. S2 in the ESI†), indicating the formation of complex **1**. 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 Fig. 3. In order to verify the nature of the product formed in the solid-state, the control reaction was also carried out in an $\text{EtOH}-\text{H}_2\text{O}$ solution. Single crystals suitable for X-ray diffraction were obtained in two weeks. 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 (see Fig. 3).

The above observations raise such questions as what is the function of acetate salt, and is H_2O_2 indispensable in the reaction? To answer these questions, control experiments were

designed and carried out. First, we observed the reaction in the absence of acetate anions. When a few drops H_2O_2 were added to the solid $[\text{Ru}(\text{H}_2\text{biim})_3](\text{PF}_6)_2$, then ground, no colour change was observed. Furthermore, when NaOAc was used instead of NH_4OAc , the reaction proceeded smoothly. However, when NH_4Cl or NaCl was used instead of NH_4OAc , powder X-ray diffraction showed that no new species formed, indicating that acetate is indispensable for the redox reaction. Second, the “liquid-assisted” solid-state reaction was performed by using a few drops of solvent such as H_2O or methanol instead of the oxidant H_2O_2 . We found that the redox reaction did take place, but very slowly. The color changed from yellow to blue after the

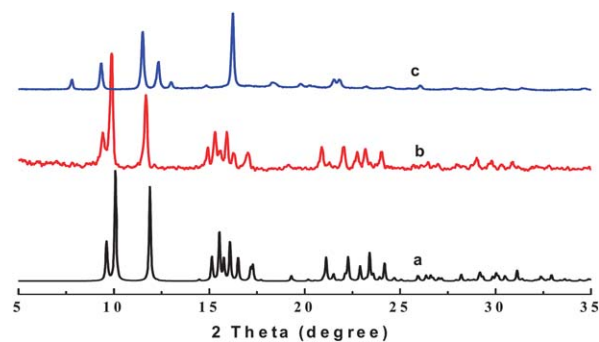


Fig. 3 Powder XRD patterns of (a) the simulation based on the single-crystal analysis of **1**, (b) the as-synthesized sample by grinding, and (c) $[\text{Ru}(\text{H}_2\text{biim})_3](\text{PF}_6)_2$.

grinding mixture was exposed to air for several days. The above observation indicates that H_2O_2 is dispensable in the reaction. That is to say, $[\text{Ru}(\text{H}_2\text{biim})_3](\text{PF}_6)_2$ can be oxidised to $[\text{Ru}(\text{Hbiim})_3]$ by oxygen in the presence of acetate anions. We know that the distal deprotonation of imidazole can reduce the redox potential of metal center.^{23–26} Our previous study showed that the addition 1 equiv of acetate to the solution of $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{biim})]^{2+}$ shifted the absorption band from 485 nm to 507 nm due to the monodeprotonation of the H_2biim ligand.²⁷ In this case, each $[\text{Ru}(\text{H}_2\text{biim})_3]^{2+}$ cation can form 6-fold robust hydrogen bonds with three acetate anions, inducing deprotonation at three sites. The increased deprotonation of the H_2biim ligands greatly increases the electron density at the Ru(II) center and shifts the oxidation potentials of the Ru(II) complex to a less positive value,²² with a final generation of $[\text{Ru}(\text{Hbiim})_3]$ species in the presence of oxygen.

To verify the potential shift of the Ru(II) complex in the presence of acetate, electrochemical measurements on $[\text{Ru}(\text{H}_2\text{biim})_3](\text{PF}_6)_2$ complex were carried out in acetonitrile solution. The oxidation potential of Ru(II)/Ru(III) negative-shifted upon addition of acetate. It shifted to 0.17 V from the original value of 0.24 V when 2 equiv of acetate anions were added (see Fig. S4 in the ESI†).

Solid-state synthesis of **2**

Furthermore, we also expanded the anion modulation solid-state reaction to the preparation of the analogous complex $[\text{Co}(\text{Hbiim})_3]$, although it has been synthesized *via* the deprotonation reaction of $[\text{Co}(\text{H}_2\text{biim})_3](\text{NO}_3)_3$ with strong base in solution.^{34,35} When the $[\text{Co}(\text{H}_2\text{biim})_3]\text{Cl}_2$ complex was used as a starting reactant instead of $[\text{Ru}(\text{H}_2\text{bbim})_3](\text{PF}_6)_2 \cdot 3\text{H}_2\text{O}$ under identical reaction conditions for the preparation of complex **1**, complex **2** was rapidly obtained, in a high yield, by manual grinding. During the course of grinding, the color changed from brown to chrysoidine (see Fig. S3 in ESI†). Powder X-ray diffraction showed the reaction product to be highly crystalline, and the reaction was quantitative, since no starting materials were detected, as shown in Fig. 4.

To clarify the structure of the product obtained from the solid-state reaction, we first compared its PXRD pattern with simulations based on the known crystal structure of $[\text{Co}(\text{Hbiim})_3] \cdot \text{CH}_3\text{CO}_2\text{Et} \cdot \text{CH}_3\text{OH}$ ³⁴ and $[\text{Co}(\text{Hbiim})_3] \cdot 0.5\text{DMF} \cdot 0.8\text{H}_2\text{O}$.³⁵ However, they are obviously different, indicating that it is a new phase. Secondly, a control reaction of $[\text{Co}(\text{H}_2\text{biim})_3]\text{Cl}_2$ with NH_4OAc in a 1 : 3 ratio was carried out in an EtOH–water solution. After volatilization of the solvent, chrysoidine colored single crystals of complex **3** were obtained in two weeks. However, its PXRD pattern is distinct from that of the as-synthesized sample prepared by grinding. It has the same cell parameters as the published complex $[\text{Co}(\text{Hbiim})_3] \cdot 0.5\text{DMF} \cdot 0.8\text{H}_2\text{O}$,³⁵ although they are prepared by different approaches concomitant with various solvents. Finally, the as-synthesized sample by grinding was dissolved in a solution of EtOH–water to grow a single crystal. Its crystal structure reveals that it is different from complex **3**, not only in unit cell parameters but also in the co-crystallized solvent molecules, although they crystallize from an identical solution. Fortunately, the observed PXRD pattern of the as-synthesized sample by grinding closely matched the theoretical PXRD pattern

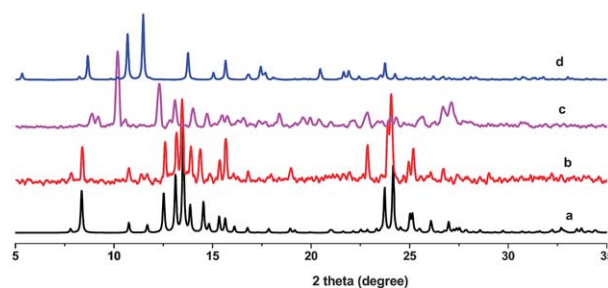


Fig. 4 Powder XRD patterns of (a) the simulation based on the single-crystal analysis of **2**, (b) the as-synthesized sample by grinding, (c) $[\text{Co}(\text{H}_2\text{biim})_3]\text{Cl}_2$, and (d) the simulation based on the single-crystal analysis of **3**.

calculated from the single crystal structure (see Fig. 4), indicating that the bulk powder had the same overall structure as its crystalline solid. 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.

It should be pointed out that the reaction products obtained from different approaches, such as the solid-state and solution reactions, and crystallization from various solvents, are different in some cases.³⁹ In $[\text{Ru}(\text{Hbiim})_3]$, the same structure was obtained from both the solid-state reaction and solutions. However, in the case of $[\text{Co}(\text{Hbiim})_3]$, complex **2** was obtained from the solid-state reaction, whereas **3** was afforded by solution reaction, although they crystallized from the same solution. Determining which factors may affect and mediate the structure and how to control the structure still remain great challenges.

Conclusions

In summary, the grinding together of the $[\text{M}(\text{H}_2\text{biim})_3]^{2+}$ species ($\text{M} = \text{Ru}$ and Co) and NH_4OAc is demonstrated as a convenient and effective preparative method for $[\text{M}(\text{Hbiim})_3]$ complexes. However, the phase obtained from the solid-state reaction may be different from that prepared from solution in some cases, even though they crystallize from an identical solution. Our results showed that the $[\text{M}(\text{H}_2\text{biim})_3]^{2+}$ ($\text{M} = \text{Ru}$ and Co) species can be oxidized to the corresponding $[\text{M}(\text{Hbiim})_3]$ species by oxygen *via* the modulation of acetate anions, due the deprotonation of the $[\text{M}(\text{H}_2\text{biim})_3]^{2+}$ species triggered by acetate anions, which greatly increases the electron density of the M(II) center and shifts the oxidation potentials of M(II) complex to a less positive value.

Experimental

Materials and physical technique

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 $400\text{--}4000\text{ cm}^{-1}$ on a Bruker TENSOR 27 FT–IR spectrometer. ^1H 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 K α radiation at a scanning rate of 4° min⁻¹ with 2 θ ranging from 5° to 50°. Thermogravimetric data were collected on a Netzsch TG-209 analyzer in nitrogen at a heating rate of 10 °C min⁻¹. Electrochemical measurements were carried out with a CHI-630C electrochemistry system in acetonitrile with Bu₄NClO₄ (0.1 M, 1 mL) as the supporting electrolyte at a scan rate of 50 mV s⁻¹. A three-electrode assembly comprising of a platinum button working electrode, a Pt auxiliary electrode, and a non-aqueous Ag/AgCl reference electrode were used. The H₂biim,⁴⁰ [Ru(H₂biim)₃](PF₆)₂·3H₂O,²¹ and [Co(H₂biim)₃]Cl₂⁴¹ were synthesized following the published procedures, respectively, and checked with elemental analysis and NMR spectroscopy.

Synthesis of [Ru(Hbiim)₃] (1)

Solid-state reaction method. A stoichiometric 1 : 3 mixture of [Ru(H₂biim)₃](PF₆)₂·3H₂O (0.1 mmol, 0.084 g) and CH₃COONH₄ (0.3 mmol, 0.025 g) was manually ground in an agate mortar for 25 min, and in this period four drops of 30% H₂O₂ (0.2 mL) were added to facilitate the reaction. The color change of the original material from yellow to blue indicated that the reaction took place over this period. After that, the product was washed with acetonitrile (1 mL), water (5 mL), and then EtOH (5 mL) under reduced pressure to remove the unreacted material and byproduct. Finally, the product was dried in air at room temperature. Yield, 98%.

Solution reaction method. CH₃COO NH₄ (0.3 mmol, 0.025 g) was added to a solution of [Ru(H₂bbim)₃](PF₆)₂·3H₂O (0.1 mmol, 0.084 g) in EtOH–H₂O (1 : 1, 15 mL). The mixture solution was stirred at room temperature for 20 min, and then filtered. The filtrate was kept at room temperature to volatilize the solvent. After two weeks, dark-blue single crystals were collected. Yield, 30%. C₁₈H₁₅N₁₂Ru (500.49): C 43.16, H 3.00, N 33.57; found C 42.76, H 2.90, N 33.17%. FT–IR data (cm⁻¹): 3430–2328 br, 1632 s, 1560 m, 1516 m, 1451 m, 1415 m, 1378 m, 1299 s, 1074 s, 849 s, 741 s, 682 m, 559 s, 472 m.

Solid-state syntheses of [Co(Hbiim)₃]·3H₂O (2)

The synthetic procedure is similar to that of solid-state synthesis of **1**, using [Co(H₂biim)₃]Cl₂ instead of [Ru(H₂biim)₃](PF₆)₂·3H₂O and washing with a mixed solution of EtOH and water (1 : 1). Yield, 83.5%. A single crystal suitable for X-ray diffraction was obtained by dissolution of the solid-state reaction product (0.035 g) in a mixed solution of EtOH and water (1 : 1, 16 mL), and volatilization of the solvent for about two weeks. C₁₈H₂₁N₁₂O₃Co (512.46): C 42.15, H 4.09, N 32.78; found C 42.75, H 3.69, N 33.18%. FT–IR data (cm⁻¹): 3460–2562 br, 1610 s, 1528 m, 1485 m, 1409 s, 1349 m, 1202 m, 1143 s, 1105 s, 757 s, 691 s, 545 m, 463 s. The TGA experiment on **2** was carried out from 30 to 800 °C. The weight loss of 10.3% in the range 30–180 °C (see Fig. S1 in the ESI†) corresponds to the loss of 3 water molecules (calculated 10.5%).

Table 1 Crystal data and structure refinement for **1**, **2** and **3**.^{a,b}

| Complex | 1 | 2 | 3 |
|---|--|---|---|
| Formula | C ₁₈ H ₁₅ N ₁₂ Ru | C ₁₈ H ₂₁ N ₁₂ O ₃ Co | C ₁₉ H ₁₈ N ₁₂ O _{0.5} Co |
| Formula weight | 500.49 | 512.40 | 480.91 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic |
| Space group | P2 ₁ /c | P2 ₁ /n | Pbcn |
| <i>a</i> (Å) | 12.2028(12) | 8.1000(8) | 12.625(1) |
| <i>b</i> (Å) | 12.6711(12) | 22.692(2) | 20.431(2) |
| <i>c</i> (Å) | 17.5676(13) | 12.0490(13) | 33.166(3) |
| β (deg) | 131.125(4) | 96.852(2) | 90 |
| <i>V</i> (Å ³) | 2046.2(3) | 2198.8(4) | 8555.0(14) |
| <i>Z</i> | 4 | 4 | 16 |
| <i>D_c</i> (g cm ⁻³) | 1.625 | 1.548 | 1.487 |
| μ (mm ⁻¹) | 0.800 | 0.830 | 0.840 |
| Data/parameters | 2906/280 | 3778/307 | 4996/587 |
| <i>R</i> ₁ (<i>I</i> > 2 σ) | 0.0398 | 0.0577 | 0.0529 |
| <i>wR</i> ₂ (all data) | 0.1033 | 0.1364 | 0.1477 |
| GOF | 1.01 | 1.01 | 1.06 |
| $\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ³) | 0.56/–0.37 | 0.41/–0.38 | 0.78/–0.44 |

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

Synthesis of [Co(Hbiim)₃]·0.5EtOH (3)

[Co(H₂biim)₃]Cl₂ (0.3 mmol, 0.159 g) and CH₃COONH₄ (0.9 mmol, 0.075 g) were added to a mixed solution of EtOH and water (1 : 1, 16 mL). The mixed solution was stirred at room temperature for 20 min, and then filtered. The filtrate was kept at room temperature to volatilize the solvent. After about 15 days, chrysoidine colored single crystals were collected. Yield, 20%. C₁₉H₁₈N₁₂O_{0.5}Co (480.91): C 47.36, H 3.74, N 34.90; found C 46.98, H 3.47, N 34.87%. FT–IR data (cm⁻¹) for **3**: 3430–2509 br, 1625 s, 1509 m, 1407 s, 1342 m, 1219 m, 1139 s, 1096 m, 914 m, 762 s, 719 m, 697 m, 545 s, 458 s.

X-Ray crystallography

Crystal data as well as details of data collection and refinement for the complexes are summarized in Table 1. Diffraction intensities were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). Absorption corrections were applied using SADABS.⁴² The structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELXS-97 and SHELXL-97 programs, respectively.⁴³ 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 molecule EtOH in **3** was highly disordered over two orientations at the measured temperature (153 K), and the hydrogen atoms on C37 and C38 were not added.

Acknowledgements

This work was supported by the NSF of China (20771104, 21071154 and 21001031) and Sun Yat-Sen University.

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