

# Toward Heteronuclear Molecular Re(I)-Cu(II) Boxes: Structural, Luminescent, and Magnetic Properties

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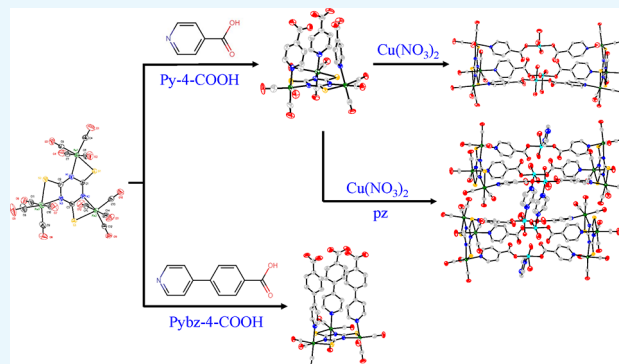
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**ABSTRACT:** The bifunctional ligands of isonicotinic acid (Py-4-COOH) and 4-pyrid-4-ylbenzoic acid (Pybz-4-COOH) instead of polypyridines were therefore reacted with  $(\text{Re}(\text{CO})_4)_3(\text{C}_3\text{N}_3\text{S}_3)$  ( $\text{C}_3\text{N}_3\text{S}_3$  = cyanurate trianion), resulting in the formation of two trinuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COOH})_3]$  (**1**) and  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Pybz-4-COOH})_3]$  (**2**), respectively. In the meantime, both complexes **1** and **2** are connected by three bifurcated hydrogen bonds between their carboxylic acid moieties Py-4-COOH and Pybz-4-COOH to form the supramolecular trigonal-prismatic and -antiprismatic structures, respectively. It is noted that complex **1** can further react with copper(II) nitrate upon deprotonation to give nonanuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_9$  (**3**), where two trinuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COO})_3]$  moieties are connected by three penta-coordinate copper(II) ions, each coordinating to two carboxylates and three water molecules, to form the trigonal-prismatic structure. Surprisingly, addition of pyrazine (pz) in the synthetic process of complex **3** resulted in serendipitous isolation of a rare example of octadecanuclear  $\{[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_6(\text{pz})_2\}_2$  (**4**), which can be regarded as a dimer of complex **3**, connected by two bridging pz ligands. Interestingly, both complexes **3** and **4** are heteronuclear molecular Re(I)-Cu(II) boxes, constructed by a complex-as-a-ligand strategy. Furthermore, complexes **1** and **2** can exhibit respective low-energy luminescence at *ca.* 561 and 534 nm at room temperature upon photoexcitation, and complex **3** is found to display antiferromagnetic coupling of  $-127.68$  and  $-134.70$   $\text{cm}^{-1}$ , possibly due to multiple hydrogen bonds inducing significant Cu(II)⋯Cu(II) coupling.



## INTRODUCTION

Extensive studies on metal-containing pyridylthiolates (pyS) have been carried out because of their structural diversities,<sup>1</sup> biological applications,<sup>2</sup> and useful precursors for related metal sulfides<sup>3</sup> as well as industrial catalysis.<sup>4</sup> Trithiocyanuric acid ( $\text{H}_3\text{C}_3\text{N}_3\text{S}_3$ ), with three N,S-donors (pyS), displays various bridging and/or chelating modes to coordinate with a large number of metal ions upon deprotonation.<sup>5</sup> Interestingly, the trianionic ligand of  $\text{C}_3\text{N}_3\text{S}_3$  moieties can act as a tridentate form by their sulfur donors or a three-chelate-bridging form by their bidentate N,S-donors. The  $\text{C}_3\text{N}_3\text{S}_3$  ligand has been successfully used to synthesize trinuclear Ru(II)- $\text{C}_3\text{N}_3\text{S}_3$  complexes of non-linear optical behavior.<sup>5a</sup> In addition, trinuclear half-sandwiched Ir(III)- and Rh(III)- $\text{C}_3\text{N}_3\text{S}_3$  complexes have been isolated and structurally determined,<sup>5b</sup> where they have been found as a co-catalyst for the polymerization of norbornene with methylaluminumoxane (MAO). Furthermore, both supramolecular capsule and trigonal-prismatic architectures built from the reaction of tris(Zn-cyclen) (cyclen = 1,4,7,10-tetraazacyclododecane) with  $\text{C}_3\text{N}_3\text{S}_3$  were reported,<sup>6</sup> and the related architectures with void spaces should hold potential to display

molecular recognition events in aqueous solution, and later, the  $\text{C}_{1-12}$  hydrocarbon encapsulation by the related Zn- $\text{C}_3\text{N}_3\text{S}_3$  cages were demonstrated as well.<sup>7</sup>

Jin and coworkers reported two unprecedented octadecanuclear macrocyclic complexes that have been constructed from the reactions of pyridyl-functionalized imidazole-4,5-dicarboxylates with  $[\text{Cp}^*\text{RhCl}_2]_2$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ).<sup>8</sup> Their crystal structures, characterized by X-ray diffraction, represented the first examples of 60-membered metal-containing macrocycles, which are composed of 18 half-sandwiched  $\text{Cp}^*\text{Rh}$  cores and six 2-(pyridin-4-yl)-1H-imidazole-4,5-dicarboxylate ligands. Jin's work demonstrated that pyridyl-substituted imidazole-4,5-dicarboxylates can be used as versatile organic linkers in the construction of both infinite networks and large discrete

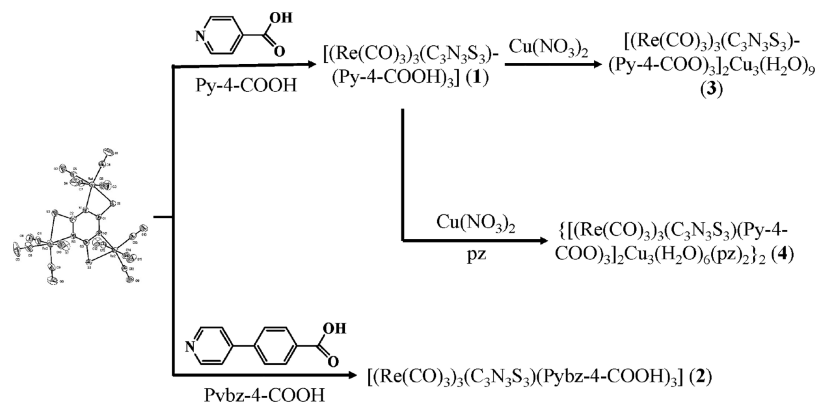
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## Scheme 1. Reaction Scheme of Complexes 1–4



architectures, i.e., a rare octadecanuclear metal-containing macrocycle. Recently, Chen and coworkers also published an interesting octanuclear zinc(II) container, namely, **1-Zn**, through the reactions of  $\text{Zn}^{2+}$ , *p*-*tert*-butylsulfonylcalix[4]arene, and pyridinium-functionalized dicarboxylate ligands.<sup>9</sup> Such a molecular container of **1-Zn** showed highly selective and sensitive recognition toward 2-picolyamine, monitored by the absorption and emission spectra. The intramolecular charge transfer (ICT) between the host and guest molecules was proposed to play a key role in the modulation of the electronic properties of the assembled host-guest adducts.

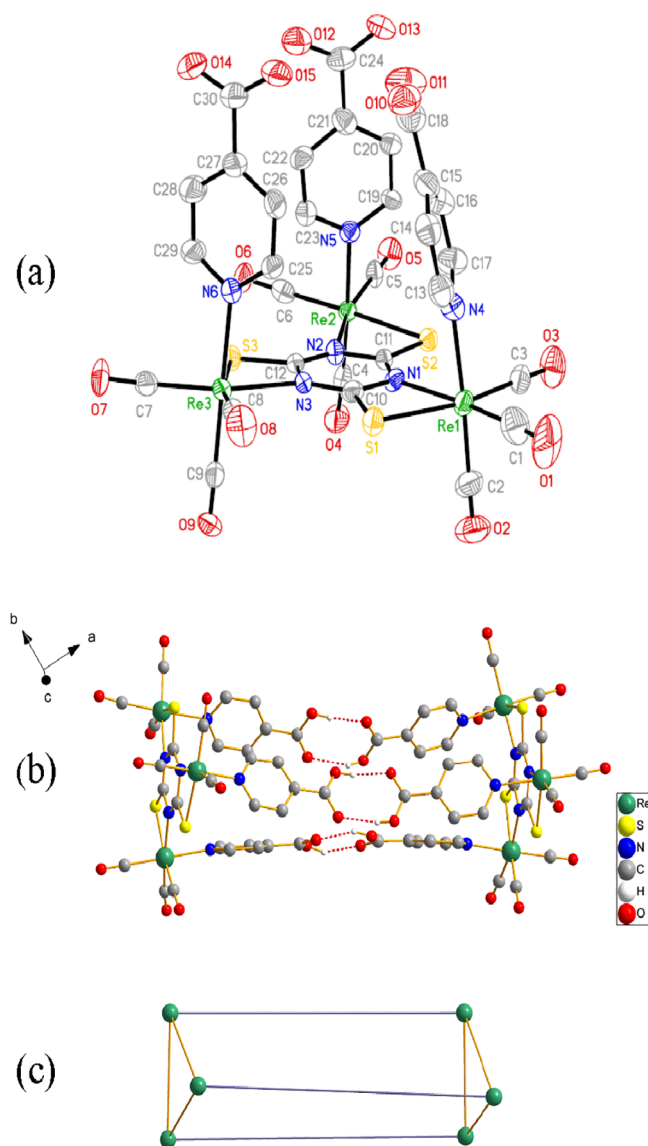
A series of molecular boxes were previously constructed based on a versatile building block of  $[(\text{Re}(\text{CO})_4)_3(\text{C}_3\text{N}_3\text{S}_3)_3]$  with various linear dipyrindyl (pyrazine (pz), 4,4'-bipyridine (bpy), 1,2-di(4-pyridyl)ethylene (dpe), bis(4-pyridyl)acetylene (bpa), and 1,4-bis(pyridyl-4-ylethynyl)benzene (bpb)) and tripyridyl (1,3,5-tris(4-pyridylethynyl)benzene (tpb)) ligands by our group.<sup>10</sup> Interestingly, various trigonal-prismatic structures of  $[(\text{Re}(\text{CO})_3)_6(\text{L})_3(\text{C}_3\text{N}_3\text{S}_3)_2]$  ( $\text{L} = \text{pz}$ , bpy, bpe, bpa, and bpb) can be systematically tuned and synthesized, and moreover, a rare nonanuclear box of  $[(\text{Re}(\text{CO})_3)_9(\text{tpb})_3(\text{C}_3\text{N}_3\text{S}_3)_3]$  involving the tripyridyl ligand (tpb) can be also isolated as a remarkable triangular-star structure.<sup>10a</sup> Furthermore, our work was also extended to molecular boxes based on two tetrapyrindyl (1,2,4,5-tetraethynyl(4-pyridyl)benzene (tpeb) and tetra(4-pyridyl)tetrathiafulvalene (TTF(py)<sub>4</sub>)) ligands, and indeed, hexanuclear  $[(\text{Re}(\text{CO})_3)_6(\text{tpeb})_2(\text{C}_3\text{N}_3\text{S}_3)_2]$  and dodecanuclear  $[(\text{Re}(\text{CO})_3)_{12}(\text{TTF}(\text{py})_4)_3(\text{C}_3\text{N}_3\text{S}_3)_4]$  boxes were afforded, respectively, while reacting with  $(\text{Re}(\text{CO})_4)_3(\text{C}_3\text{N}_3\text{S}_3)$ .<sup>10b</sup> Two tetrapyrindyl ligands with different core units resulting in quite different assembled products have been observed. We report herein that the bifunctional ligands of isonicotinic acid (Py-4-COOH) and 4-pyrid-4-ylbenzoic acid (Pybz-4-COOH) were reacted with  $(\text{Re}(\text{CO})_4)_3(\text{C}_3\text{N}_3\text{S}_3)$ , leading to two respective trinuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COOH})_3]$  (1) and  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Pybz-4-COOH})_3]$  (2). It is noted that  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COOH})_3]$  can further react with copper(II) nitrate upon deprotonation, leading to nonanuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_9 \cdot 4\text{CH}_3\text{OH}$  (3) through the complex-as-a-ligand strategy, where two trinuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COO})_3]$  moieties are connected by three penta-coordinate copper(II) ions to form the heteronuclear trigonal prism. Surprisingly, addition of pyrazine (pz) in the above synthetic process led to serendipitous isolation of a rare octadecanuclear box of  $\{[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_6(\text{pz})_2\}_2$  (4). In addition to the solid-state

luminescence for complexes 1 and 2, the magnetic study for complex 3 is also reported.

## RESULTS AND DISCUSSION

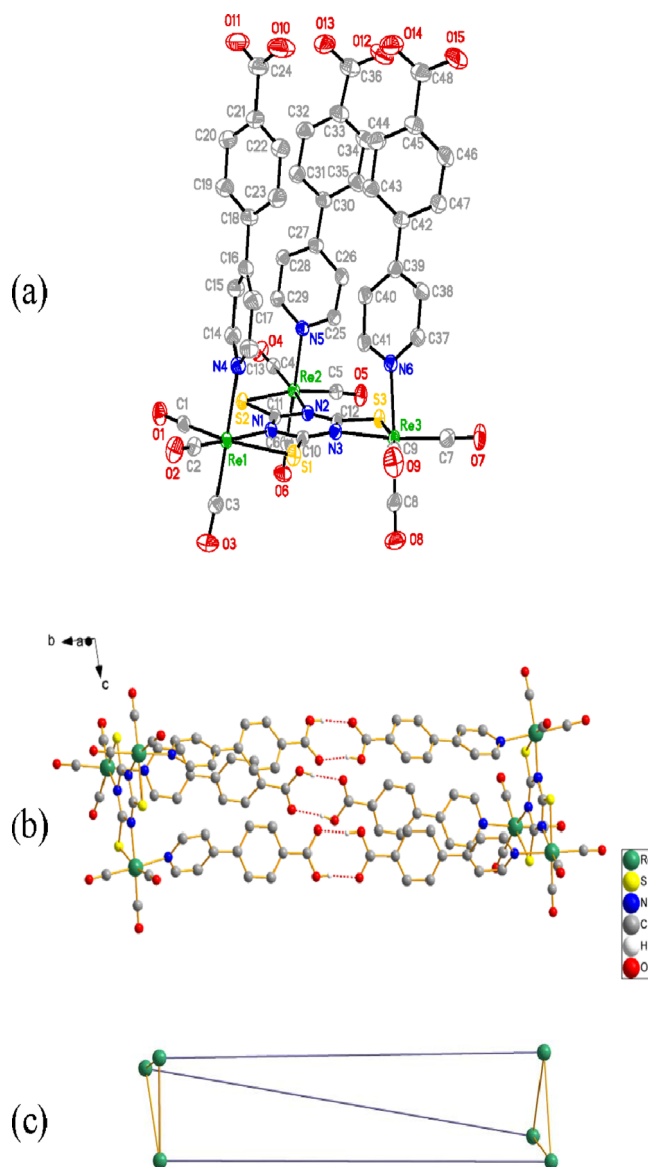
The bifunctional ligands of isonicotinic acid (Py-4-COOH) and 4-pyrid-4-ylbenzoic acid (Pybz-4-COOH) can be reacted with  $(\text{Re}(\text{CO})_4)_3(\text{C}_3\text{N}_3\text{S}_3)$ , leading to the formation of two respective trinuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COOH})_3]$  (1) and  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Pybz-4-COOH})_3]$  (2) in solvothermal reactions, which are connected by three bifurcated hydrogen bonds between their carboxylic acid moieties Py-4-COOH and Pybz-4-COOH to form the trigonal prism or antiprism. It is noted that  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COOH})_3]$  (1) can further react with copper(II) nitrate upon deprotonation, leading to nonanuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_9 \cdot 4\text{CH}_3\text{OH}$  (3) through the complex-as-a-ligand strategy, where two trinuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COO})_3]$  moieties are connected by three penta-coordinate copper(II) ions to form the heteronuclear trigonal prism. Surprisingly, a rare octadecanuclear box of  $\{[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_6(\text{pz})_2\}_2$  (4) can be serendipitously isolated in the synthetic process of complex 3 with pyrazine (pz), which can be regarded as a dimer of complex 3, connected by two bridging pz ligands. Unfortunately, this crystal-growing process cannot give a pure phase of complex 4 at this moment and thus prevents it from further characterizations. The reaction scheme is shown in Scheme 1.

**Description of Crystal Structures.** Complex 1 exhibits a trinuclear structure and its dimeric hydrogen-bonded diagram as shown in Figure 1a,b, respectively, which crystallized in the space group of *Pna*2<sub>1</sub>. The trinuclear complex 1 contains one  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3]$  moiety and three Py-4-COOH ligands sitting on the same side, where each Py-4-COOH coordinates with the Re(I) ion through the pyridine donor and leaves the carboxylic acid intact. The Re(I) ion, in an octahedral geometry, contains three carbonyl groups in a facial arrangement, one bidentate N,S-donor of the  $\mu_3$ - $\text{C}_3\text{N}_3\text{S}_3$  ligand, and one nitrogen atom from the Py-4-COOH ligand. In complex 1, two  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)_3]$  moieties form a supramolecular trigonal-prismatic structure through three bifurcated hydrogen bonds between their carboxylic acid moieties Py-4-COOH (i.e.,  $\text{O}\cdots\text{O}$  2.585 (18)–2.711 (16) Å), and the simplified supramolecular trigonal prism is shown in Figure 1c, where each hydrogen-bonded dimer contains an intramolecular  $\text{Re}(\text{I})\cdots\text{Re}(\text{I})_{\text{av}}$  separation of 6.04 Å as well as a dihedral angle of 4.14°



**Figure 1.** (a) Crystal structure of complex 1 with the ORTEP diagram showing 50% probability of ellipsoids, (b) the dimeric hydrogen-bonded diagram, and (c) its simplified supramolecular trigonal prism.

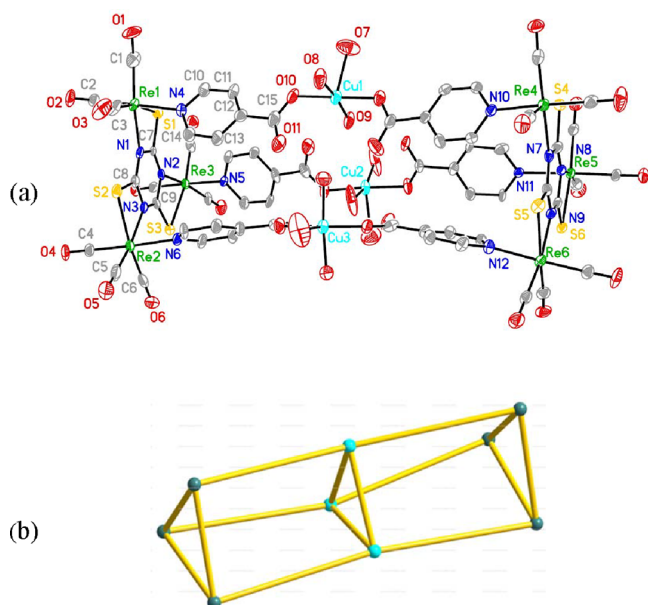
between the two Re(I) triangles. The dihedral angle of  $4.14^\circ$  is comparable to the values of  $0.57\text{--}3.33^\circ$  found in  $[(\text{Re}(\text{CO})_3)_6(\text{L})_3(\text{C}_3\text{N}_3\text{S}_3)_2]$ ,<sup>10</sup> indicative of almost a parallel trigonal prism. Moreover, the length of the trigonal prism within a hydrogen-bonded dimer is calculated to be *ca.* 16.49 Å for the centroid...centroid separation of two triazine rings of  $\text{C}_3\text{N}_3\text{S}_3$  ligands. Complex 2 shows a similar structural motif as that of complex 1, except that Py-4-COOH was replaced by Pybz-4-COOH, and its trinuclear structure, dimeric hydrogen-bonded diagram, and simplified supramolecular trigonal prism are shown in Figure 2a,c, respectively. Unlike complex 1, two  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)]$  moieties form a supramolecular trigonal-antiprismatic structure through three bifurcated hydrogen bonds between their carboxylic acid moieties, Pybz-4-COOH (i.e.,  $\text{O}\cdots\text{O}$  2.577(4)–2.700(4) Å) for complex 2. Each hydrogen-bonded dimer contains an intramolecular  $\text{Re}(\text{I})\cdots\text{Re}(\text{I})_{\text{av}}$  separation of 6.04 Å and a dihedral angle of  $4.28^\circ$  between the two Re(I) triangles, which are similar to those of complex 1 and our reported cages,<sup>10</sup> indicative of almost a



**Figure 2.** (a) Crystal structure of complex 2 with the ORTEP diagram showing 50% probability of ellipsoids, (b) the dimeric hydrogen-bonded diagram, and (c) its simplified supramolecular trigonal prism.

parallel trigonal-antiprismatic structure as well. In addition, the length of the trigonal antiprism within a hydrogen-bonded dimer is calculated to be *ca.* 25.22 Å for the centroid...centroid separation of two triazine rings of  $\text{C}_3\text{N}_3\text{S}_3$  ligands.

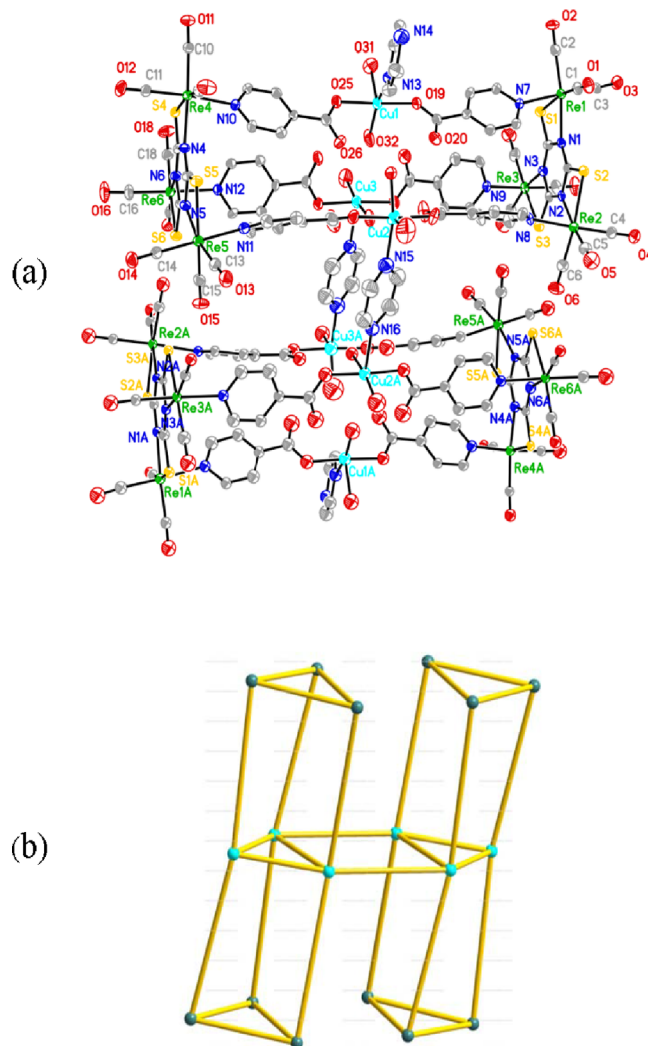
Complex 3 displays a heteronuclear trigonal-prismatic structure and a simplified trigonal prism, shown in Figure 3a,b, respectively, which crystallized in the space group of  $P2_12_12_1$ . The nonanuclear complex 3 contains two  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)]$  moieties, six Py-4-COO ligands, and three penta-coordinate Cu(II) ions, where each Cu(II) ion coordinates with two Py-4-COO ligands through carboxylate donors in a *trans* configuration and coordinates with three water molecules to adopt a square-pyramidal geometry. The apical water molecules have Cu(II)–O distances of 2.290(5)–2.336(6) Å, whereas the other Cu(II)–O distances from water molecules and carboxylates are within 1.929(5)–1.986(5) Å. The former show significantly longer distances than the latter, indicative of typical Jahn–Teller distortion for the  $d^9$ -metal Cu(II) ion. As a heteronuclear trigonal prism, complex 3 is



**Figure 3.** (a) Crystal structure of complex 3 with the ORTEP diagram showing 50% probability of ellipsoids and (b) its simplified trigonal prism.

composed of two Re(I) and one Cu(II) triangles having intramolecular Re(I)⋯Re(I)<sub>av</sub> and Cu(II)⋯Cu(II)<sub>av</sub> separations of 6.05 and 5.36 Å, respectively. Indeed, the Cu(II)⋯Cu(II) distances of 5.355 (2)–5.421 (2) Å within the Cu(II) triangle are too long to consider the interactions in the solid state since they are dramatically longer than the sum of van der Waals radii of 2.8 Å. However, hydrogen bonds between coordinated water molecules (i.e., O⋯O 2.586 (12)–2.790 (3) Å) would be anticipated to compensate for such long Cu(II)⋯Cu(II) distances, and hence the antiferromagnetic interactions can be observed and will be discussed in the following section. Moreover, the length of the heteronuclear trigonal prism is calculated to be *ca.* 17.92 Å for the centroid⋯centroid separation of two triazine rings of C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> ligands.

Complex 4 shows a double trigonal-prismatic structure and its simplified trigonal prism in Figure 4a,b, respectively, which crystallized in the space group of *P2<sub>1</sub>/n*. In fact, complex 4 can be regarded as a dimer of complex 3, connected by two bridging pyrazine (pz) ligands, and its heteronuclear octadecanuclear structure contains 4 [(Re(CO)<sub>3</sub>)(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)] moieties, 12 Py-4-COO ligands, 6 penta-coordinate Cu(II) ions, and 2 bridging and 2 terminal pz ligands. There are three different coordination environments for Cu(II) ions (i.e., Cu(1), Cu(2), and Cu(3)), which all adopt a square-pyramidal geometry as those of complex 3. Cu(1) ion coordinates with two Py-4-COO ligands through carboxylate donors in a *trans* configuration and also coordinates with two water molecules and one terminal pz ligand, where one water molecule sits at an apical position with a Cu(1)–O(31) distance of 2.222 (12) Å, indicative of typical Jahn–Teller distortion, and one terminal pz ligand sits at the equatorial position with a Cu(1)–N(13) distance of 2.013 (12) Å. Cu(2) and Cu(3) ions show similar coordination environments, except that one water molecule is at an apical position for the former (Cu(2)–O(34), 2.274 (14) Å) and the bridging pz ligand is at an apical position (Cu(3)–N(16), 2.290 (13) Å) for the latter, which are indicative of typical Jahn–Teller distortion as well. Moreover, the Cu(2) ion coordinates with another bridging pz ligand having a Cu(2)–N(15) distance of 2.116



**Figure 4.** (a) Crystal structure of complex 4 with the ORTEP diagram showing 30% probability of ellipsoids and (b) its simplified double trigonal prism.

(16) Å, which is obviously longer than the Cu(1)–N(13) distance of 2.013 (12) Å with the terminal pz ligand, but it is significantly shorter than the Jahn–Teller distorted Cu(3)–N(16) distance of 2.290 (13) Å. The remaining Cu(II)–O distances from water molecules and carboxylates are within 1.907 (11)–1.954 (8) Å, which are comparable to those of 1.929 (5)–1.986 (5) Å in complex 3. The heteronuclear double trigonal prism of complex 4 is also composed of four Re(I) and two Cu(II) triangles having intramolecular Re(I)⋯Re(I)<sub>av</sub> and Cu(II)⋯Cu(II)<sub>av</sub> separations of 6.05 and 5.31 Å, respectively. Again, the Cu(II)⋯Cu(II) distances of 5.307 (3)–5.448 (3) Å are too long to consider the interactions in the solid state since they are dramatically longer than the sum of van der Waals radii of 2.8 Å. However, hydrogen bonds between coordinated water molecules (i.e., O⋯O, 2.590 (2)–2.674 (2) Å) can be observed. In addition, the length of the heteronuclear trigonal prism is calculated to be *ca.* 18.18 Å for the centroid⋯centroid separation of two triazine rings of C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> ligands, which is similar to that of complex 3 (i.e., 17.92 Å).

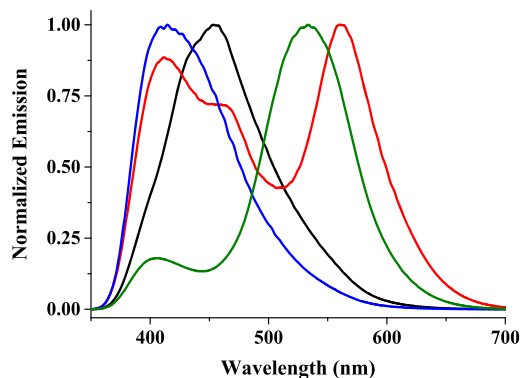
Re–N and Re–S bond distances corresponding to C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> are within 2.154 (9)–2.217 (12) and 2.503 (4)–2.555 (4), 2.160 (3)–2.183 (3) and 2.533 (1)–2.545 (1), 2.159 (5)–2.181 (5)

and 2.527 (2)–2.561 (2), and 2.161 (9)–2.201 (9) and 2.525 (3)–2.548 (3) Å, and Re–N<sub>pyridyl</sub> bond distances are within 2.189 (10)–2.237 (10), 2.208 (3)–2.227 (3), 2.208 (4)–2.233 (5), and 2.199 (10)–2.227 (9) Å for complexes 1–4, respectively. The respective C–S bond distances of 1.677 (11)–1.731 (15), 1.705 (3)–1.707 (3), 1.692 (6)–1.713 (6), and 1.678 (11)–1.709 (11) Å for complexes 1–4 are mostly within a similar range of 1.690 (10)–1.704 (10) Å in the trinuclear Ru(II)–C<sub>3</sub>N<sub>3</sub>S<sub>3</sub> complexes,<sup>5a</sup> 1.713 (7) Å in [(CuPPh<sub>3</sub>)<sub>6</sub>(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>2</sub>],<sup>13</sup> and those in our reported Re(I) cages,<sup>10</sup> suggestive of a C=S bond (thione) character and some C–S bond (thiolate) character. In fact, they are longer than the 1.6564 (19) Å distance in [Cu(H<sub>3</sub>C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)Cl]<sub>n</sub><sup>14</sup> and 1.651 (6)–1.662 (6) Å in a co-crystal structure of [(H<sub>3</sub>C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>2</sub>:4,4'-bipy:C<sub>6</sub>H<sub>6</sub>],<sup>15</sup> both with the typical C=S bond character, whereas the above values are shorter than the typical C–S bond of 1.829 (26) Å in alkanethiolates.<sup>16</sup>

**Powder X-ray Diffraction Studies and Thermogravimetric Analysis.** The powder X-ray diffraction (PXRD) patterns of complexes 1–3 mostly matched with those of simulated patterns, where pure phases for the solid samples are suggested (Figure S1–S3). However, some minor differences are still observed between the as-synthesized and simulated ones, which are most likely ascribed to the partial loss of solvates for complexes 1 and 2 or the squeezed data for complex 3.

To check the thermal stabilities of complexes 1–3, thermal gravimetric analyses (TGA) were recorded (Figure S4–S6). The TGA analysis of complex 1 shows that no weight loss was observed until 115 °C (the solvates of 1.5C<sub>7</sub>H<sub>8</sub> and 0.25CH<sub>3</sub>CN are possibly lost from their crystal lattice before the measurement). After this temperature, a large weight loss is observed, which is suggestive of decomposition. Complex 2 shows a weight loss of 3.9% (calculated, 4.3%) at 150 °C, corresponding to the loss of four benzene molecules, followed by another weight loss of 4.1% (calculated, 4.0%) at 315 °C, corresponding to the loss of two DMF molecules. A significant weight loss after 315 °C occurs, suggestive of the decomposition as well. For complex 3, there is only a one-step weight loss of 10.5% (calculated, 9.5%) until 215 °C, corresponding to the loss of four CH<sub>3</sub>OH and nine coordinated H<sub>2</sub>O molecules, and it starts to decompose after this temperature.

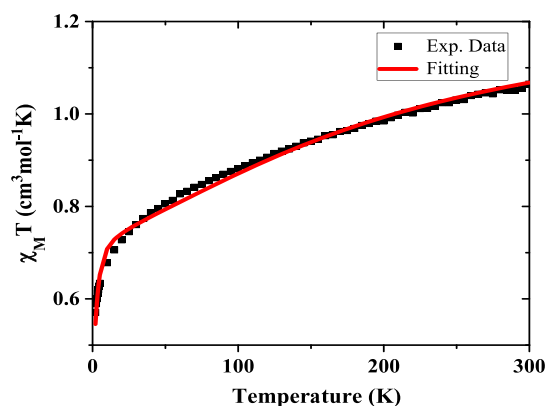
**Solid-State Emission Spectra.** Since only solid samples of complexes 1 and 2 are emissive, their emission spectra with the Py-4-COOH and Pybz-4-COOH ligands at room temperature are shown in Figure 5. Upon photoexcitation at 325 nm, both



**Figure 5.** Normalized emission spectra of Py-4-COOH (black line), Pybz-4-COOH (blue line), complex 1 (red line), and complex 2 (green line) at room temperature. The excitation is at 325 nm.

complexes 1 and 2 show emissions with maxima at *ca.* 411, 462, and 561 nm and 406 and 534 nm, respectively. The emissions for Py-4-COOH and Pybz-4-COOH were also measured at room temperature, exhibiting respective emission maxima at *ca.* 455 and 415 nm, respectively. The high-energy emissions at *ca.* 411 and 462 nm and 406 nm for complexes 1 and 2, respectively, are most probably ascribed to an intraligand (IL) transition since they show high similarities to those of Py-4-COOH and Pybz-4-COOH. It is noted that the low-energy emissions at *ca.* 561 and 534 nm for complexes 1 and 2, respectively, are suggestive of a metal-to-ligand charge-transfer (MLCT) transition in origin, where similar assignments have been made in our previous dipyriddy, tripyridyl, and tetrapyriddy systems.<sup>10</sup>

**Magnetic Properties.** The magnetic susceptibility data of complex 3 were obtained by applying a magnetic field of 1000 G in the temperature range of 2 to 300 K on a ground crystalline sample. The  $\chi_M T$  vs  $T$  plot of complex 3 is illustrated in Figure 6.



**Figure 6.** Plot of  $\chi_M T$  vs  $T$  for complex 3.

According to the structure of complex 3, three Re(I) ions should have a low-spin  $d^6$ -electron configuration so to provide diamagnetic centers. Therefore, the magnetic susceptibilities are supposed to be from three Cu(II) ions. Indeed, the  $\chi_M T$  value of complex 3 at 300 K is 1.06 cm<sup>3</sup> mol<sup>-1</sup> K. This value is close to, but somewhat lower than, the ideal spin-only value of 1.125 cm<sup>3</sup> mol<sup>-1</sup> K for three uncoupled Cu(II) ions, which implies that the antiferromagnetic coupling can be seen even at 300 K. Upon cooling, the  $\chi_M T$  values decrease with the decrease in temperatures and then reach 0.591 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K. Judging from the structure, three Cu(II) ions are resembled close to an isosceles. Hence, the formula of eq 1<sup>17</sup> was applied to fit the  $\chi_M T$  vs  $T$  plot, where  $J$  represents the magnetic coupling between two equal laterals and  $J'$  is the coupling between the two bottom Cu(II) ions. Reasonable good fitting was obtained by eq 1, giving  $g = 2.14$ ,  $J = -127.68$  cm<sup>-1</sup>, and  $J' = -134.70$  cm<sup>-1</sup>, and the result was shown by the red solid line in Figure 6. Recalling the structure of complex 3, the intramolecular Cu(II)···Cu(II) distances are in the range of 5.355 (2)–5.421 (2) Å, which do not support such strong antiferromagnetic coupling purely by the super-exchange interactions. By detailed analysis of the structure, solid hydrogen bond networks are found among the Cu(II) ions. We therefore can plausibly suggest that the hydrogen-bonded networks are the main driving forces for the antiferromagnetic coupling between Cu(II) ions.

$$H = -2J(S_1 \cdot S_3 + S_2 \cdot S_3) + 2J' \cdot S_1 \cdot S_2 \quad (1)$$

## CONCLUSIONS

A trinuclear Re(I) complex of  $(\text{Re}(\text{CO})_4)_3(\text{C}_3\text{N}_3\text{S}_3)$  has been previously reacted with the bidentate, tridentate, and tetradentate polypyridines under solvothermal conditions, resulting in the formation of a series of molecular boxes by self-assembly reactions.<sup>10</sup> In continuing with the above synthetic approach, the bifunctional ligands of isonicotinic acid (Py-4-COOH) and 4-pyrid-4-ylbenzoic acid (Pybz-4-COOH) instead of polypyridines are reacted with  $(\text{Re}(\text{CO})_4)_3(\text{C}_3\text{N}_3\text{S}_3)$ , leading to two trinuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COOH})_3]$  (**1**) and  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Pybz-4-COOH})_3]$  (**2**), respectively. In the meantime, both complexes **1** and **2** are connected by three bifurcated hydrogen bonds between their carboxylic acid moieties of Py-4-COOH and Pybz-4-COOH to form the supramolecular trigonal-prismatic and -antiprismatic structures, respectively. It is noted that complex **1** can further react with copper(II) nitrate upon deprotonation to give nonanuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_9$  (**3**), where two trinuclear  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COO})_3]$  moieties are connected by three penta-coordinate copper(II) ions, each coordinating to two carboxylates and three water molecules, to form the trigonal-prismatic structure. Surprisingly, addition of pyrazine (pz) in the synthetic process of complex **3** resulted in serendipitous isolation of a rare example of octadecanuclear  $\{[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_6(\text{pz})_2\}_2$  (**4**), which can be regarded as a dimer of complex **3**, connected by two bridging pz ligands. Interestingly, both complexes **3** and **4** are heteronuclear molecular Re(I)-Cu(II) boxes, which are successfully constructed by a complex-as-a-ligand strategy, with Cu(II)⋯Cu(II) distances of 5.355 (**2**)–5.421 (**2**) and 5.307 (**3**)–5.448 (**3**) Å, respectively. Furthermore, complexes **1** and **2** can exhibit respective low-energy luminescence at *ca.* 561 and 534 nm at room temperature upon photoexcitation, and complex **3** is found to display antiferromagnetic couplings of  $-127.68$  and  $-134.70$  cm<sup>-1</sup>, possibly due to multiple hydrogen bonds instead of long Cu(II)⋯Cu(II) distances, inducing significant Cu(II)⋯Cu(II) coupling.

## EXPERIMENTAL SECTION

### General Information and Physical Measurements.

Trithiocyanuric acid ( $\text{H}_3\text{C}_3\text{N}_3\text{S}_3$ ), isonicotinic acid (Py-4-COOH), 4-pyrid-4-ylbenzoic acid (Pybz-4-COOH), and pyrazine (pz) were purchased from Aldrich Chemicals, and  $\text{Re}_2(\text{CO})_{10}$  was purchased from Strem Chemicals. All solvents (analytical grade) for synthesis were used without further purification. The infrared (IR) spectra were recorded with samples in the form of KBr pellets on a PerkinElmer PC 16 FTIR spectrometer. The solid-state emission spectra at room temperature and at 77 K were recorded on a Hitachi F-7000 spectrophotometer. The powder X-ray diffraction (PXRD) data were recorded on a Bruker D2 Phaser with  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å and a scan speed of  $2^\circ(2\theta)/\text{min}$  as well as a  $2\theta$  range of  $2$ – $60^\circ$ . Thermal gravimetric analysis (TGA) measurements were performed using a PerkinElmer STA6000 thermal analyzer. Elemental analysis (EA) of the complexes was performed on an Elementar vario EL III Heraeus CHNOS Rapid F002 elemental analyzer, and the solid samples were pre-treated by subjecting to vacuum overnight.

$[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COOH})_3] \cdot 1.5\text{C}_7\text{H}_8 \cdot 0.25\text{CH}_3\text{CN}$  (**1**,  $1.5\text{C}_7\text{H}_8 \cdot 0.25\text{CH}_3\text{CN}$ ).  $[(\text{Re}(\text{CO})_4)_3(\text{C}_3\text{N}_3\text{S}_3)]$  (5.4 mg, 0.005 mmol) and isonicotinic acid (Py-4-COOH; 1.9 mg, 0.015 mmol) were stirred in a toluene (4.0 mL)/ $\text{CH}_3\text{CN}$  (0.05 mL)

solution for 10 min in air, and the mixture was transferred to a 25 mL Teflon reactor, sealed, and heated in an oven to  $80^\circ\text{C}$  for 48 h. After cooling, orange crystals were obtained and then filtered, washed with *n*-hexanes, and dried in air with *ca.* 40.6% yield (3.05 mg). Anal. Calcd (%) for  $\text{C}_{39}\text{H}_{20}\text{N}_{12}\text{O}_{19}\text{Re}_6\text{S}_6$  (**1**,  $1.5\text{C}_7\text{H}_8 \cdot 0.25\text{CH}_3\text{CN}$ ): C, 32.76; H, 1.86; N, 5.83. Found: C, 32.49; H, 1.82; N, 5.93. FT-IR:  $\nu_{\text{C}=\text{O}}$ , 2025, 1906 cm<sup>-1</sup>;  $\nu_{\text{C}=\text{O}}$ , 1718 cm<sup>-1</sup>;  $\nu_{\text{C}=\text{N}/\text{C}=\text{O}}$ , 1559, 1449 cm<sup>-1</sup>.

$[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Pybz-4-COOH})_3] \cdot 2.25\text{C}_6\text{H}_6 \cdot \text{DMF}$  (**2**,  $2.25\text{C}_6\text{H}_6 \cdot \text{DMF}$ ).  $[(\text{Re}(\text{CO})_4)_3(\text{C}_3\text{N}_3\text{S}_3)]$  (5.4 mg, 0.005 mmol) and 4-pyrid-4-ylbenzoic acid (Pybz-4-COOH; 3.0 mg, 0.015 mmol) were stirred in a benzene (4.0 mL)/DMF (0.05 mL) solution for 10 min in air, and the mixture was transferred to a 25 mL Teflon reactor, sealed, and heated in an oven to  $100^\circ\text{C}$  for 48 h. After cooling, orange crystals were obtained and then filtered, washed with *n*-hexanes, and dried in air with *ca.* 31.8% yield (2.91 mg). Anal. Calcd (%) for  $\text{C}_{54}\text{H}_{37}\text{N}_7\text{O}_{16}\text{Re}_3\text{S}_3$  (**2**,  $0.5\text{C}_6\text{H}_6 \cdot \text{DMF}$ ): C, 38.26; H, 2.20; N, 5.79. Found: C, 38.43; H, 1.97; N, 5.50. FT-IR:  $\nu_{\text{C}=\text{O}}$ , 2024, 1906 cm<sup>-1</sup>;  $\nu_{\text{C}=\text{O}}$ , 1702 cm<sup>-1</sup>;  $\nu_{\text{C}=\text{N}/\text{C}=\text{O}}$ , 1609, 1449 cm<sup>-1</sup>.

$[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_9 \cdot 4\text{CH}_3\text{OH}$  (**3**,  $4\text{CH}_3\text{OH}$ ).  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COOH})_3]$  (13.5 mg, 0.01 mmol) dissolved in methanol (3.0 mL) was transferred onto a DI water solution (3.0 mL) of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (4.9 mg, 0.02 mmol) with  $\text{CH}_3\text{OH}$  and DI water (1:1, 3.0 mL) as a buffer layer. Green crystals with *ca.* 13.0% yield (4.11 mg) were obtained by a layer method for 5 days. Anal. Calcd (%) for  $\text{C}_{60}\text{H}_{42}\text{Cu}_3\text{N}_{12}\text{O}_{39}\text{Re}_6\text{S}_6$  (**3**,  $4\text{CH}_3\text{OH}$ ): C, 23.95; H, 1.65; N, 5.82. Found: C, 23.59; H, 1.39; N, 5.50. FT-IR:  $\nu_{\text{C}=\text{O}}$ , 2023, 1904 cm<sup>-1</sup>;  $\nu_{\text{C}=\text{O}}$ , 1717 cm<sup>-1</sup>;  $\nu_{\text{C}=\text{N}/\text{C}=\text{O}}$ , 1623, 1559, and 1448 cm<sup>-1</sup>.

$\{[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COO})_3]_2\text{Cu}_3(\text{H}_2\text{O})_6(\text{pz})_2\}_2$  (**4**).  $[(\text{Re}(\text{CO})_3)_3(\text{C}_3\text{N}_3\text{S}_3)(\text{Py-4-COOH})_3]$  (13.5 mg, 0.01 mmol) and pyrazine (pz; 2.4 mg, 0.03 mmol) were dissolved in methanol (3.0 mL)/acetone (1.0 mL) and transferred onto a DI water solution (3.0 mL) of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (2.5 mg, 0.01 mmol) with  $\text{CH}_3\text{OH}$  and DI water (1:1, 3.0 mL) as a buffer layer. Green crystals were obtained by a layer method for 5 days. Unfortunately, this crystal-growing process cannot give a pure phase at this moment and thus prevents it from further characterizations.

**X-ray Crystallography.** Suitable crystals were mounted on glass capillaries and the data collection was then carried out on a Bruker SMART CCD diffractometer with Mo radiation (0.71073 Å). A preliminary orientation matrix and its unit cell parameters were determined from 3 runs of 15 frames, with each frame corresponding to  $0.3^\circ$  scan in 20 s, followed by spot integration and least-squares refinement. The crystal data were therefore measured using an  $\omega$  scan of  $0.3^\circ$  per frame for 20 s until a complete hemisphere had been collected. Later, cell parameters were retrieved using SMART<sup>11(a)</sup> software and refined with SAINT<sup>11(b)</sup> on all observed reflections. The data reduction was performed with the SAINT software and corrected for the Lorentz and Polarization effects. Furthermore, absorption corrections were applied with the program SADABS.<sup>11(c)</sup> Finally, the structures were solved by direct methods with the SHELXS-97<sup>11(d)</sup> program and refined by full-matrix least-squares methods on  $F^2$  with SHELXL-2014/7.<sup>11(e)</sup> The data collection and refinement details of complexes **1**–**4** are summarized in Table S1, and their crystal data are deposited in CCDC 2102084–2102087.

**Magnetic Susceptibility Measurements.** Magnetic susceptibility measurements were carried on a Quantum Design

MPMS7 system. Samples were restrained with eicosane to prevent torquing. The background signals caused by the gel cap and eicosane were calibrated by blank measurements. The diamagnetism contributions from the sample were calculated by Pascal's constants.<sup>12</sup> Measurements were performed at the National Taiwan University Instrument Centre, College of Science.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c05638>.

- Crystallographic data of compound 1 (CIF)
- checkCIF/PLATON report for compound 1 (PDF)
- Crystallographic data, PXRD patterns, and TGA traces (PDF)

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### Notes

The authors declare no competing financial interest.

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