Inorganic Chemistry

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[Cu{SC(O)O[']Pr}]₉₆: A Giant Self-Assembled Copper(I) Supramolecular Wheel Exhibiting Photoluminescence Tuning and Correlations with Dynamic Solvation and Solventless Synthesis

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ABSTRACT: The hierarchical self-organization of structurally complex high-nuclearity metal clusters with metallosupramolecular wheel architectures that are obtained from the self-assembly of smaller solvated cluster units is rare and unique. Here, we use the potentially heteroditopic monothiocarbonate ligand and demonstrate for the first time the synthesis and structure of a solvated non-cyclic hexadecanuclear cluster $[Cu{SC(O)O^iPr}]_{16}$ ·2THF (1) that can simultaneously desolvate and self-assemble in solution and subsequently form a giant metallaring, $[Cu{SC(O)O^iPr}]_{96}$ (2). We also demonstrate a luminescent precursor to cluster (2) can be achieved through a solventless and rapid mechanochemical synthesis. Cluster (2) is the highest nuclearity copper(I) wheel and the largest metal cluster containing a heterodichalcogen (O, S) ligand reported to date. Cluster (2) also exhibits solid-state luminescence with relatively long emission lifetimes at 4.1, 13.9 (μ s). The synthetic strategy described here opens new research avenues by replacing solvent molecules in stable {Cu₁₆} clusters with designed building units that can form new hybrid and multifunctional finite



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supramolecular materials. This finding may lead to the development of novel high-nuclearity materials self-assembled in a facile manner with tunable optical properties.

1. INTRODUCTION

Polynuclear metal clusters with metallaring or wheel structures attract interest due to their unique physico-chemical properties and structural aesthetics.¹ In 1990, single-strand molecular wheels^{2,3} were first reported for $[Cr_8F_8(O_2C'Bu)_{16}]$ and $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$, and since then, the pursuit of new wheel-type structures with different nuclei and both low and high nuclearities have been ongoing.^{4–10} The multiple-strand cluster wheel {Mn₈₄} has been described,¹¹ while Müller and co-workers did pioneering work on high-nuclearity {Mo₁₅₄} and {Mo₁₇₆} clusters.^{12,13} The majority of reported wheel structures have been obtained from hard O-donor ligands while the heavier chalcogenide S-donor ligands are notably scarce and of lower nuclearity as signified by the clusters Ni₁₀,¹⁴ Ni₂₀,¹⁵ Co₁₂,¹⁶ Ni₁₂,¹⁶ and Fe₁₄. The chemistry of clusters with coordination by *solvated*

The chemistry of clusters with coordination by *solvated* ligands has been investigated, and these systems have solvated ligands in the first coordination sphere of the metal. But such systems are comparatively rare and distinguish themselves from the numerous examples where the solvated molecules are in the second coordination sphere of the metal center essentially for the purpose of filling void space. Forty years ago, Johnson and Lewis did pioneering work on clusters of the type $[Os_3(CO)_{11}(NCMe)]$ that can react with a variety of ligands L $(L = CO, PPh_3, etc.)$ to produce clusters such as $[Os_3(CO)_{11}L]$ but noticed the cluster nuclearity remain

unchanged.¹⁸ More recently, Zacchini et al. reported interesting solvent displacement reactions on a di-solvated bimetallic Fe-Cu carbido carbonyl cluster [Fe₄C(CO)₁₂{Cu-(MeCN)₂ with N-donor ligands (quinoline and phenanthroline).¹⁹ From these results, we speculated whether a cluster could desolvate a coordinating ligand, followed by an in situ self-assembly process by filling the coordination vacancy with a cluster unit, instead of a ligand. If successful, this strategy would lead to large nuclearity clusters but also perhaps form structures heretofore unobtainable without the aid of selfassembly. Here, we describe such a system for the first time. The work continues our long-term interest in dichalcogenbased clusters of the group 11 metals (Cu, Ag, Au) that contain a closed-shell d^{10} electron configuration. Such systems are targeted due to their combined potential of large cluster formation and rich photochemistry.^{20,21,22}

There are only a few complexes known with the monothiocarbonate (MTCO) ligand, $[SC(O)OR]^-$. They

Received: March 20, 2021 Published: June 3, 2021





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exhibit non-wheel and mononuclear structures, including iron,²³ manganese,²⁴ tungsten,²⁵ ruthenium,²⁶ zinc,²⁷ cadmi-um,²⁷ copper,²⁸ and gold²⁸ complexes. Wheel structures reported for S/O-systems are restricted to the group 11 metals (Cu, Ag, Au) and contain mainly hard O-donor ligands; metal wheels containing S-donor ligands are few and of lower nuclearity. A low-nuclearity ring structure for {Cu₆} has been reported.²⁹ To the best of our knowledge, no supramolecular wheel structure for silver is known. The gold clusters $\{Au_{36}\}^3$ and {Au18}³¹ display the highest nuclearities known for Sbased wheel structures. Wheel-shaped clusters have intrinsic complexity, and control of the self-assembly process to purposefully form a wheel motif is a non-trivial challenge: the outcome typically relies on serendipity rather than a systematic synthetic protocol. For example, Cronin and coworkers explored the symmetry, structure, and self-assembly mechanism of a large seven-fold symmetric $\{Pd_{84}\}$ multiple-strand wheel.^{32,33} The highly complex polyoxopalladate structure containing 84 palladium centers was synthesized in a reaction similar to the reaction that produced a smaller {Pd₁₅} wheel,³⁴ and the only variable reaction parameter was temperature, demonstrating strict control of reaction conditions is necessary to obtain reproducible results. Systematic studies on comparable large clusters remain elusive and are unknown for Cu-based systems.

We recently reported an interesting class of emissive disolvated hexadecanuclear Cu(I) clusters of the type $[Cu{SC-(O)OC_6H_{11}}]_{16}$ ·2(acetone) obtained from the reaction between $K[SC(O)OC_6H_{11}]$ and $[Cu(MeCN)_4](PF_6)$ in acetone and also demonstrated that the luminescence can be tuned with various N-donor ligands.³⁵ That study highlighted a number hypotheses to further investigate, specifically: (i) the role of bulky vs non-bulky ligands in cluster formation, (ii) the role of a non-bulky ligand in cluster stabilization and different coordination modes, (iii) the role of coordinating solvents in the self-assembly of clusters, (iv) formation of clusters under solventless conditions and comparison to solution chemistry, and (v) structure–(optical) property correlations.

2. RESULTS AND DISCUSSION

2.1. Synthesis, Solventless Synthesis, and Characterization. To probe the structural stabilization and to modify

the luminescence of this system, we proposed that similar solvated clusters should be accessible for different coordinating solvents (acetone, CH₃CN, THF) to form an extended family. In an attempt to mitigate steric clash and increase flexibility, we opted for a less bulky chelating ligand, anticipating that it may affect the structure of the final product and lead to new types of luminescent materials. We subsequently investigated the reaction between $K[SC(O)OCH(CH_3)_2]$ and $[Cu(MeCN)_4]$ - (PF_6) in THF solvent (molar ratio 1:1) which formed the solvated cluster $[Cu{SC(O)OCH(CH_3)_2}]_{16}$ ·2THF (1). Significantly, when the same reaction was carried out in acetone, we were pleasantly surprised by the discovery of a nano-sized supramolecular wheel $[Cu{SC(O)OCH(CH_3)_2}]_{96}$ (2). We also probed the optical properties of the reaction proceeding through simple manual grinding (mechanochemical synthesis) under ambient conditions over a few minutes, vide infra. The reactions are summarized in Scheme 1.

The less bulky isopropyl monothiocarbonate ligand thus appeared to play a key role in the formation of the large $\{Cu_{96}\}$ ring cluster. Both the formation and the structure of the $\{Cu_{96}\}$ ring were achieved by the dynamics of solvation and steric effects of six self-assembled $\{Cu_{16}\}$ units. Importantly, the synthesis strategy allows one to adjust both the choice of solvent and the level of steric hindrance and, hence, gain better control over the result of the formed product. The choice of solvent in this system plays a critical role in the synthesis of the {Cu₉₆} supramolecular wheel since only the solution synthesis in acetone was successful using nonbulky ligands; the inhibition of further growth from $\{Cu_{16}\}$ to $\{Cu_{96}\}$ in THF solvent is likely due to the greater degree of coordinating ability of THF to Cu(I) centers. Conversely, the steric hindrance caused by bulky cyclohexyl groups prevented formation of the {Cu₉₆} cluster. Thus, while bulky groups restrict the formation of the $\{Cu_{96}\}$ cluster, the comparatively poor coordinating ability of acetone increases the stability of a higher aggregation state as evident from the X-ray crystal structure.

The synthesis of $[Cu_{16}\{S(O)COC_6H_{11}\}_{16}]\cdot 2(acetone)$ can be achieved under solvent-free conditions by grinding together the starting materials, $[Cu(CH_3CN)_4]PF_6$ and $K[S(O)-COC_6H_{11}]$, for only 1 min; presumably, the bulky cyclohexyl group prevents forming a larger cyclic cluster.³⁵ This pubs.acs.org/IC



Figure 1. Attempted mechanochemical solventless synthesis of (2) by a grinding method: (a) mixture of Cu(I) and ligand before grinding under UV light, (b) mixture after 2–3 min under UV light, contains luminescent precursor product and KPF₆, (c) solid-state luminescence image after KPF₆ removal.



Figure 2. FTIR spectra of copper MTCO (K[S(O)CO'Pr]) reaction products after washing with water (blue) and after chloroform extraction (red), and crystals of (2) (black).

observation made us consider whether the synthesis of (2) can be performed solventless with a less bulky ligand. When $[Cu(CH_3CN)_4]PF_6$ and K[S(O)CO'Pr] were ground together in a 1:1 ratio without solvent or added heat, free stoichiometric amounts of CH_3CN liquid were released, and it immediately resulted in the formation of a yellow paste as the acetonitrile ligands dissociated from the Cu(I) starting material (Figure 1). Neither the free monothiocarbonate ligand nor the Cu(I) salt emits under UV exposure (either in solution or solid state), and the yellow emission under UV light suggested the formation of a new Cu(I) complex. The paste showed yellow luminescence when placed under a UV lamp (365 nm) at 77 K (Figure S1).

We recorded an FTIR spectrum of starting $[Cu(CH_3CN)_4]$ -PF₆ and found the expected $\nu(C\equiv N)$ peaks at around 2300 and 2275 cm⁻¹ (Figure S2). The paste was subjected to mild heat treatment to evaporate the acetonitrile overnight, and the subsequent FTIR spectrum of the pale-yellow solid showed no trace of any acetonitrile related stretching vibrations. From this result, we conclude that the solid-state mechanochemical synthesis does not lead to a solvated form of {Cu₁₆}. (acetonitrile), but subsequent FTIR results also could not unambiguously claim the formation of cluster (2), but rather a luminescent {Cu₉₆} precursor. Removal of KPF₆ byproduct was done by either (i) washing of the air-dried residue with deionized water or (ii) extraction with chloroform. Recrystallization of both products from acetone/hexane yielded crystalline $[Cu{S(O)CO'Pr}]_{960}$ cluster (2). When the residue from mechanosynthesis was washed with water, the copper monothiocarbonate product remained undissolved. The FTIR spectrum of this solid was recorded (blue trace in Figure 2) to determine whether the Cu₉₆ cluster (black trace in Figure 2) forms directly from mechanosynthesis, or only upon dissolution and recrystallization from acetone.

The FTIR spectra of the mechanosynthesis product and the chloroform extract matched the spectrum of crystals of (2) very closely between 3000 and 820 cm⁻¹ (black trace in Figure 2), but the mechanosynthesis product (blue trace) also contained bands at lower frequencies that are not present in the spectrum of (2). This suggested that, although it appeared some complexation occurred during grinding, it cannot be concluded that the Cu₉₆ wheel formed directly during solventfree synthesis but presumably formed a precursor because the FTIR spectrum of the residue obtained after drying the chloroform extract (red trace) was nearly identical to that of the Cu₉₆ crystals, and we concluded that dissolution of the mechanochemical product in chloroform allowed isolation of the Cu_{96} wheel. The band corresponding to the C=O stretching vibration in $K[S(O)CO^{i}Pr]$ appeared at 1585 cm⁻¹ (Figure S3), whereas, in the Cu_{96} wheel, two C=O stretching

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bands were observed at 1620 and 1698 cm⁻¹ (Figure S4). These two bands indicate two different coordination modes for the $[S(O)CO^{i}Pr]^{-}$ ligand with significantly different C=O bond lengths after coordination to Cu(I) centers. We also followed the solid-state reaction by powder XRD, but the results are inconclusive as it showed an amorphous product.

The ¹H and ¹³C NMR spectra of $K[S(O)CO^{i}Pr]$ (Figures S5 and S6) were recorded in D_2O due to poor solubility of the salt in organic solvents. The single C-O-CH proton resonated as a quintet at 4.77 ppm (Figure S7a), and the methyl protons resonated as a doublet at 1.14 ppm (Figure S7b). The ¹H NMR spectrum of (1) was recorded in CDCl₃; therefore, the chemical shifts of the two compounds cannot be directly compared. Nonetheless, the ¹H NMR spectrum is useful for confirming the presence of $[S(O)CO^{i}Pr]^{-}$ in both the clusters (1) and (2) (Figures S8 and S9). The methyl protons in (1) resonated at 1.29 ppm (doublet), and the C-O-CH proton resonated as a broad singlet at 4.94 ppm. The chemical shifts of the isopropyl -C-O-CH proton appeared at 4.94 (1) and 4.95 ppm (2). The methyl protons resonated as a doublet at 1.97 ppm (1, 2), and (1) additionally revealed two proton signals at 1.78 and 3.61 ppm for the coordinated THF molecules. The ESI-MS for (1) was not informative, whereas the positive-ion ESI mass spectrum of (2) displayed a peak at m/z 2943.7 (calcd 2944.1) assignable to the [{CuSC(O)- $OCH(CH_3)_2\}_{16} + Na]^+$ unit (Figure S10). Because of the structural similarity of the chemical environments between the Cu₁₆ units and the Cu₉₆ cluster, the NMR peaks of the ligands corresponding to these two systems become indistinguishable. Unambiguous confirmation of the formation of the Cu₁₆ and Cu₉₆ clusters were obtained from X-ray crystallographic analysis.

2.2. Molecular Structures. The crystals suitable for X-ray diffraction analysis were grown from THF (1) and acetone (2). The crystal parameters are listed in Table S1. The solvated cluster (1) is structurally related to the reported $[Cu{SC(O)-OC_6H_{11}}]_{16}$ ·2(acetone).³⁵ A perspective view of cluster (1) together with the atomic labeling of Cu atoms is shown in Figure 3a.

Cluster (1) contains a bowl-shaped core structure in which three pentanuclear copper units (a square pyramid unit flanked by two extended butterfly units) are fused together and are coordinated by monothiocarbonate ligands. The apex and base of the central square pyramidal unit are defined by the atoms (Cu8) and (Cu6, Cu7, Cu10, and Cu11) (see Figure 3b). The body and wingtip atoms of the extended butterflies flanking the central square pyramidal unit are occupied by (Cu1, Cu4) (Cu16, Cu15) and (Cu2, Cu3) (Cu13, Cu14), respectively. Importantly, the Cu atom (Cu9) is solvated by two THF molecules and positioned at the base of the central square pyramid unit. The Cu_{16} clusters are all solvated at the (Cu9) atom, and the solvation prevents further cluster growth. This atom position thus plays a key role in understanding how $6 \times$ ${Cu_{16}}$ units self-assemble to form the ${Cu_{96}}$ cluster through a solvated-unsolvated equilibrium that we refer to as dynamic solvation. All the Cu(I) atoms including the peculiar (Cu9) atom are held together through a combination of trimetallictriconnective (κ^{3} : μ_{2} -S, μ -O), tetrametallic-tetraconnective (κ^4 : μ_3 -S, μ -O), and trimetallic-triconnective (κ^3 : μ_3 -S) binding modes from 16 monothiocarbonate ligands. The Cu-S and Cu–O distances of 1 have values ranging from 2.197(12) to 2.390(10) Å and 2.049(3) to 2.406(3) Å, respectively. The Cu-S-Cu, S-Cu-S, O-Cu-S, and O-Cu-O bond angles



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Figure 3. Single-crystal X-ray structure of $[Cu{SC(0)OCH-(CH_3)_2}]_{16}$ ·2THF. Hydrogen atoms are omitted for clarity.

are in the order of 70.45(4)-137.01(5), 102.12(4)-165.58(5), 104.31(9)-110.95(10), and $70.66(6)-77.08(10)^\circ$. Further, cluster 1 is stabilized by cuprophilic interactions, that were manifested by Cu···Cu distances in the range of 2.595(7)-3.041(7) Å (Figure 3a), typical of that found in an earlier reported system.³⁵ The Cu···Cu bond distances are notably shorter than the sum of van der Waals radii (3.92 Å) between the Cu centers. The dihedral angle between the wing planes of the butterflies ranges from 77.61° to 84.17° .

Single crystals of cluster (2) were grown using liquid-liquid diffusion. Pale yellow hexagonal-shaped crystals (Figure S11) appeared on the walls of the vial within 2 days, and single crystals suitable for SCXRD were removed and mounted on the diffractometer after 2 weeks. Cluster 2 crystallized in the trigonal $R\overline{3}$ space group. The total structure is neutral and comprises of 96 copper(I) ions stabilized by 96 isopropyl monothiocarbonate ligands. The cluster crystallizes in the comparatively rare S₆ virtual point group symmetry. The asymmetric unit consisted of a single $[Cu_{16}{S(O)CO'Pr}_{16}]$ subunit (Figure 4), and the trigonal unit cell contained 18 asymmetric units arranged into 3 Cu₉₆ metal wheels, each with 6 $[Cu_{16}{S(O)CO'Pr}_{16}]$ subunits (see Figure 5).

The structure of the Cu₁₆ asymmetric unit was similar to that of the hexadecanuclear complex previously reported.³⁵ The Cu₁₆ asymmetric unit (bowl-shaped core) in the Cu₉₆ cluster follows the similar structural discussion as in 1 with the removal of the solvated THF molecules coordinated to the Cu9 atom in the hexadecanuclear complex being the only distinct difference. A notable point is that one of the trimetallic-triconnective bridging (κ^3 : μ_2 -S, μ -O) ligands that coordinate to the extended butterfly motif in (1) has expanded its connecting pattern to a tetrametallic-tetraconnective (κ^4 : μ_3 -S, μ -O) mode in (2), in order to covalently link the Cu9 atom to another {Cu₁₆} building unit. In this way, six units are



Figure 4. Bowl-shaped Cu_{16} core structure that represents the asymmetric unit of the Cu_{96} cluster (2). Cuprophilic interactions with $Cu(I)\cdots Cu(I)$ distances shorter than the van der Waals radii are shown as orange bonds; black lines indicate $Cu(I)\cdots Cu(I)$ distances larger than 3.92 Å.



Figure 5. Molecular structure (left) of $[Cu{S(O)CO'Pr}]_{96}$ (isopropyl groups of the ligands omitted for clarity) and (right) the $[Cu{S(O)CO'Pr}]_{16}$ asymmetric unit (isopropyl groups shown as wireframes).

interconnected through Cu9-S15 covalent bonds, closing up a giant Cu_{96} supramolecular wheel-type structure (Figure 5); the inner-core contains a novel 36-membered {Cu₁₈S₁₈} ring. The unique architectural arrangement facilitated by the strong covalent bonds between six $\{Cu_{16}\}$ units leads to the spontaneous self-assembly of a wheel structure, presumably with more flexibility and larger stability as compared to the individual building units. It should be noted that this phenomenon is distinctly different from the Johnson and Lewis system for $[Os_3(CO)_{11}(NCMe)]$ and the Zacchini system for $[Fe_4C(CO)_{12}{Cu(MeCN)}_2]$ where the solvated ligand is simply substituted by other Lewis bases while retaining the nuclearity.^{18,19} It is worth noting that Zacchini et al. isolated high-nuclearity cyclic dimers [{Fe₄C(CO)₁₂Cu₂(μ -X) $_{2}$]^{*n*-} when bases (X = phenylthiolate, pyrazolate, (*n* = 2), or diphenolate (n = 4)) are utilized. In cluster (2), the Cu-S bond lengths vary from 2.196(2) to 2.402(15) Å and the Cu-O bond lengths are shorter in the range of 2.139(4) - 2.351(4)Å. The Cu-S-Cu, S-Cu-S, O-Cu-S, and O-Cu-O bond angles are in the order of 69.61(5)-141.46(9), 106.52(5)-141.32(6), 91.12(16)-114.50(12), and 74.16(6)-79.26(15)°, respectively. Unsurprisingly, all the bond length and angle parameters are in close agreement with those of (1). One of the dihedral angles (83.15°, 89.01°) in the butterfly showed significant deviation from (1), presumably due to the greater extent of interaction between various Cu₁₆ building units via Cu-S bonds.

The solid-state structure **2** reveals the existence of significant intramolecular cuprophilic (Cu···Cu) interactions (Figure 4).

The three pentanuclear Cu units in the Cu16 asymmetric unit were joined together through short Cu(I)…Cu(I) contacts: Cu5…Cu6 (2.691 Å) and Cu11…Cu12 (2.678 Å). Both of these Cu(I)…Cu(I) bond distances are significantly shorter than 3.92 Å, the sum of the van der Waals radii of two Cu atoms. Other Cu(I)…Cu(I) interactions were observed in the butterfly motifs that flanked the central square bipyramid, and these bond distances ranged from 2.634 to 2.861 Å. The Cu… Cu interactions in **2** are comparable to that of **1**. A recent review proposed that cuprophilic interactions are considered to be present when the Cu(I)…Cu(I) bond distances are 2.4–2.8 Å,³⁶ and thus all Cu(I)…Cu(I) interactions shown in orange in Figure 4 are cuprophilic interactions.

A summary of the MTCO coordination modes observed in (2) is shown in Figure 6. The trimetallic-triconnective $\kappa^3:\mu_2$ -S,



Figure 6. Coordination modes of MTCO ligands in Cu(I) complexes observed in the study.

 μ -O mode is similar to what has been described in smaller Cu(I) and Ag(I) monothiocarbamate complexes,^{37,38} but the large 36-membered Cu–S ring is by far the largest of its kind reported to date.

The tetrametallic-tetraconnective $\kappa^4:\mu_3$ -S, μ -O has not been described for any coinage metal complexes to date. Indeed, the MTCO ligand adopted previously unknown coordination modes to Cu(I) centers and the combination of these modes allows for the assembly of the unusual {Cu₁₆} bowl-shaped cluster. Henkel and co-workers reported a 4-membered Cu(I) butterfly architecture that transformed to a 12-membered double wheel by switching from μ_2 - to μ_3 -sulfur bridging mode and presumably improved the coordination around Cu(I) centers.³⁹

When the same Cu(I) precursor reacts with xanthate or dithiocarbamate dichalcogen ligands (two similar C–S bond lengths), also in a 1:1 molar ratio, it is worth mentioning that only low-nuclearity clusters such as Cu₄ or Cu₆ form. It is for this reason that we propose the small, but significant, variation in bond length between C–O and C–S in the monothiocarbonate ligand used here has a definitive role to play in forming a large wheel architecture in (2), a feature that can presumably be further exploited with related hetero-donor bidentate ligands. We also propose that the {Cu₉₆} cluster can potentially be an interesting example of a "magic number" ring (such as Mn₈₄ and Mo₁₅₄)^{11,12} since the overall cluster nuclearity or magic number (N = 96) is the multiplication of the symmetry number (S = 6) and building-block nuclearity (n = 16).

Gupta *et al.* showed that the acetone molecules coordinated to Cu9 in $[Cu_{16}{S(O)COC_6H_{11}}_{16}] \cdot 2OC(CH_3)_2$ are labile and can be replaced by N-donor ligands such as 2,2'-bipyridine.³⁵ We found that reduction in the bulkiness of the alkyl group in the MTCO ligand led to the formation of a metal wheel consisting of six Cu₁₆ units, where the Cu₁₆ units



Figure 7. Structural representation of the Cu_{96} wheel held together by a series of Cu-S bonds. (a) Cu-S ring shown in ball-and-stick style with the rest of the cluster drawn as a wireframe. (b) The "inner" butterfly, consisting of Cu12-Cu16 was the site where the link to Cu9′ (Cu9 of an adjacent Cu₁₆ core) occurred by bridging through the S atom of an MTCO ligand.

were joined *via* Cu–S bonds between Cu9 and an S atom in a neighboring Cu₁₆ core (Figure 7). Reduction in steric bulk of the $\kappa^3:\mu_2$ -S, μ -O ligand that bridged Cu12, Cu15, and Cu16 in the "inner" butterfly motif allowed the S atom in this ligand to bridge to the Cu9 atom of a neighboring Cu₁₆ core and adopt a $\kappa^4:\mu_3$ -S, μ -O bonding mode. The hexameric Cu₉₆ wheel appears to be held together by a series of Cu–S bonds.

When crystals of (1) were exposed to small amounts of acetone solvent, it converted to (2) within 7–10 days, and the process was reversible when crystals of (2) were added to THF (Figure 8). This was confirmed by indexing the unit cell



Figure 8. Reversible conversion between $\{Cu_{96}\}$ and $\{Cu_{16}\}$ units caused by a dynamic solvation system.

parameters (Figure S12). The proposed mechanism for this conversion remains unclear but seems unlikely to be a bona fide solid-state crystal-to-crystal transformation.

2.3. Crystal Structure and Porosity of {Cu₉₆}. The {Cu₉₆} wheels crystallized in stacks perpendicular to the *c*-axis. The distance between least-squares planes of adjacent wheels within a stack (calculated using all non-C,H atoms) was 1.6 nm (Figure 9d). This space was occupied by the isopropyl tails of the monothiocarbonate ligands. Each vertex of the unit cell represents the center of a {Cu₉₆} wheel (represented in green in Figure 9). Two other {Cu₉₆} wheels were located inside the unit cell (shown in violet and blue in Figure 9); each of these

wheels represents another stack parallel to the stacks centered on the *c*-axis.

The internal cavity of the ring has a diameter of about 10.3 Å (Figure S13), while copper-to-copper atom distances in diagonally opposite positions reach an average of ca. 18 Å. The Cu₉₆ wheel formed solvent-accessible channels when the ${Cu_{96}}$ wheels stacked on top of one another. The solvent channels had a "bead-on-string" structure, with a diameter of ~18 Å at the widest point, and ~10 Å at the narrowest point (Figure 10a). Void analysis in Mercury also revealed solvent pockets within the crystal structure (Figure 10b), though these isolated pockets are not solvent-accessible after crystallization. A solvent mask (using PLATON SQUEEZE)⁴⁰ was applied during structure refinement in Olex2 to detect and analyze residual electron density in the crystal voids. The total solventaccessible volume per unit cell was 12862.2 ${\rm \AA}^3$ (23.1% of the total unit cell volume), and the total solvent electron count per unit cell was 1207.2. This void volume is similar to what is typically seen in metal-organic framework (MOF) structures that have found applications in gas (particularly hydrogen or methane) storage,^{41,42} sensing,⁴³ and catalysis.⁴⁴ Like most MOFs, cluster (2) is also microporous (pore dimensions < 2nm). Microporous materials are sometimes classified into two sub-classes: ultramicroporous (pores smaller than 7 Å) and supermicroporous (7-20 Å) materials,⁴⁵ and (2) can therefore be considered a supermicroporous material and the solventaccessible channels could potentially be suitable for gas storage applications.

2.4. Solid-State Luminescence Properties. The attempted mechanochemical synthesis of (2) involved grinding together K[S(O)COⁱPr] and [Cu(CH₃CN)₄]PF₆ (neither are luminescent) with a mortar and pestle to form a yellow paste. This paste was weakly emissive at room temperature and highly emissive after being cooled in liquid nitrogen. The solid-state photoluminescence spectrum of this paste (Figure 11) revealed that the maximum emission was observed, $\lambda_{max} = 530$ nm, with a shoulder at 567 nm.



Figure 9. Single-crystal structure of (2) viewed (a) along the *a*-axis, (b) along the *b*-axis, and (c) along the *c*-axis. (d) A schematic representation of the layered structure, as seen in (a). The Cu_{96} wheels in the same plane in the crystal lattice are represented in the same color.



Figure 10. Porous structure of (2). (a) Cross section of the bead-on-a-string-type channel that formed parallel to the *c*-axis; the inner surface of the channel is indicated in brown and the outer surface in yellow. (b) Unit cell viewed along the *c*-axis, with pockets and solvent-accessible channels circled in black.



Figure 11. Solid-state photoluminescence spectrum of paste, directly after grinding.

The luminescent paste was purified and recrystallized, and the solid-state photoluminescence spectrum of the crystalline material was recorded for comparison (Figure 12). The excitation λ_{max} of the crystalline material (which was confirmed by SCXRD to be the pure {Cu₉₆} wheel structure) was redshifted to 372 nm, and a distinct shoulder peak was observed at 412 nm. The emission λ_{max} of the crystalline material was at 539 nm.

Gupta et al. indicated that the core structure of the $\{Cu_{16}\}$ cluster is likely susceptible to distortions when the outer ligand environment is changed, and this may explain the changes in the luminescence spectra observed after recrystallization. Crystal packing interactions have been shown to affect emission properties of other complexes,⁴⁶ and it is possible that the $\{Cu_{16}\}$ core structure experienced distortions upon crystallization, which in turn affected the luminescence.

The sensitivity of the emission behavior of the Cu_{16} core structure was further demonstrated by apparent solvatochromic behavior that was observed during purification. After grinding, the dried residue was taken up in chloroform and filtered to remove KPF₆. The solvent was removed *in vacuo*, and the residue was dried before the photoluminescence



Figure 12. Solid-state photoluminescence spectrum of crystals of (2) at room temperature.

spectrum was recorded (green curves in Figure 13). The residue was then redissolved in acetone, the solvent was



Figure 13. Solid-state photoluminescence spectra of (2) after extraction using chloroform (green) and acetone (blue).

removed *in vacuo*, and the residue dried. The photoluminescence spectrum of the solid was re-recorded (blue curves in Figure 13).

When the solid was obtained from a chloroform solution, the excitation λ_{max} was 375 nm and the emission λ_{max} was 532 nm. In contrast, the solid that was obtained from acetone solution had excitation and emission maxima at 360 and 540 nm. The excitation and emission maxima are summarized in Table S2. The data in Table S2 indicate that the emission of (2) before and after chloroform extraction was not significantly changed, although there was a significant shift in the excitation maximum. Once the sample was dissolved in acetone, the emission maximum shifted from ~530 nm to ~540 nm. As discussed, we suspect that formation of the $\{Cu_{96}\}$ wheel structure did not occur directly during grinding based on FTIR data. Exposure to acetone, however, clearly influenced the emission behavior of the cluster, regardless of whether the sample was crystallized or simply dried. We suggest that the entrapment of solvent molecules in the \sim 1.0 nm wide pores in

the $\{Cu_{96}\}$ wheels caused distortions in the core structure of the complex, which influenced the cluster-centered excited state energy and changes in emission behavior of (2).

The solid-state photoluminescence (PL) of clusters [Cu- $\{SC(O)OCH(CH_3)_2\}_{16}$ ·2THF (1) and $[Cu\{SC(O)OCH (CH_3)_2$]₉₆ (2) was also investigated at variable temperatures (Figure S14, top and bottom). Both clusters display yellow emission upon exposure to UV radiation in the solid state. Interestingly, at lower temperatures, the Cu₉₆ cluster exhibited solution state photoluminescence as well (Figure S15). The solid-state emission maximum (λ_{max}) for the complexes (1, 2)appeared at ca. 570 nm(1) and 575 nm(2), whereas the solidstate excitation spectra appeared broad with a maximum (λ_{max}) at ca. 345 nm (1) and 350 nm (2), respectively. No obvious shift in the PL spectrum of the clusters was observed upon cooling to liquid nitrogen temperatures, but the intensity did gradually increase. Large Stokes shifts in the range of 225 nm $(\sim 11 441 \text{ cm}^{-1})$ (1) and 222 nm $(\sim 11 180 \text{ cm}^{-1})$ (2) between the excitation and emission wavelengths for the clusters suggest a large distortion that occurred in the excited state. The lifetime measurement for (2) was recorded, and the relatively long emission lifetimes 4.1, 13.9 (μ s) are consistent with those expected for a spin-forbidden transition in correlated metal clusters. On the basis of our report for $[Cu{SC(O)OC_6H_{11}}]_{16} \cdot 2C_3H_6O$ and some earlier reports on Cu(I) clusters derived from chalcogen ligands, the emission can be tentatively assigned to originate from a mixture of ligand-to-metal charge-transfer (LMCT) transitions and cluster centered emission state CC with metal-centered 3d⁹4s¹ transitions, with contributions from $\text{Cu}{\cdots}\text{Cu}$ interactions. 34,47 Interestingly, the Cu-Cu distances of the Cu(I) clusters described here are comparable with those of polynuclear Cu(I) clusters that exhibit photoluminescent behavior at wavelengths greater than 500 nm.⁴⁸⁻⁵³

3. CONCLUSIONS

To conclude, we demonstrated that it is possible for a fair-sized $\{Cu_{16}\}$ nuclearity cluster to be stabilized and isolated through appropriate solvation that occurs at a key metal center on the cluster. We showed that this phenomenon is dependent on both the size of the MTCO derivative and the strength (Lewis basicity) of the solvated molecule. Next, we showed that, in appropriate solvent (acetone), the $\{Cu_{16}\}$ core can desolvate, and even in a potential coordinating solvent (acetone) present in huge excess, it instead self-assembles with another desolvated cluster present in far less quantity, once the desolvation occurs by leaving coordination vacancies around the copper center. This inevitably leads to a much larger cluster, and because the choice of ligand is inherently unsymmetrical with different C-O and C-S bond lengths, we suspect this is the main reason why the net effect is a wheel structure that forms. Here, we demonstrated that a large metal cluster of 96 copper(I) atoms can be stabilized by the monothiocarbonate ligand (L), forming a neutral Cu₉₆L₉₆ cluster. The Cu₉₆L₉₆ cluster formed in solution as a result of the self-assembly of six smaller $\{Cu_{16}\}$ units and adopts the structure of a supramolecular wheel. The intricate solvationdesolvation interplay (dynamic solvation) appears to be the key to understanding the self-assembly process. We also performed the synthesis via a mechanochemical solventless (green) route under ambient conditions but cannot say with certainty if the {Cu₉₆} cluster formed directly based on FTIR results. It is clear, however, that the formed product is luminescent and a precursor to forming $\{Cu_{96}\}\$ in a rapid fashion through simple recrystallization, and this is subject to further investigation. The new $Cu_{96}L_{96}$ cluster is highly emissive in the solid state. The formation of large clusters with supramolecular wheel structures derived from the dynamic solvation of smaller cluster units spells out a new strategy for the design of stable clusters with multifunctionality and with potential gas storage applications.

4. EXPERIMENTAL SECTION

4.1. Materials and Instrumentation. Hexafluorophosphoric acid, KOH, and Cu₂O were purchased from Sigma-Aldrich and used without further purification. Acetone, acetonitrile, chloroform, and diethyl ether were purchased from Honeywell. Hexane was purchased from ACE Chemicals. Propan-2-ol was purchased from Merck. $[Cu(CH_3CN)_4]PF_{6}$, carbonyl sulfide gas, and $K[SC(O)OCH-(CH_3)_2]$ ligand were prepared using slight modifications of literature methods. ^{52–54}

Solvents were purified following standard protocols. All reactions were performed in oven-dried Schlenk glassware using standard inert atmosphere techniques. All reactions were carried out under a N₂ atmosphere by using standard Schlenk techniques. ¹H NMR spectra were recorded on a Bruker Advance DPX300 FT-NMR spectrometer operating at 300 MHz, and the chemical shifts (δ) are reported in ppm. FTIR spectra were recorded on a PerkinElmer spectrophotometer with samples prepared as KBr pellets. Melting points were measured by using a Fargo MP-2D melting point apparatus. The elemental analyses were performed using a PerkinElmer 2400 CHN analyzer. Emission spectra were recorded using a Cary Eclipse B10 fluorescence spectrophotometer.

4.2. Synthesis. Synthesis of K[SC(O)OCH(CH₃)₂]. A mixture of 2propanol (35 mL, excess) and finely powdered KOH (18.35 g, 0.328 mol) was stirred at 40 °C for 1 h. After cooling the solution to ambient temperature, 5 mL of deionized H₂O was added to dissolve remaining solids. COS gas was generated in a separate flask using a method adapted from that described by Demselben.⁵⁴ Briefly, a stock solution of 55% (w/w) $\rm H_2SO_4$ was prepared using 98% $\rm H_2SO_4$ and deionized water. To generate an excess of COS (g), 142.66 g (0.4 mol) of this stock solution was added to KSCN (38.87 g, 0.4 mol) and the mixture was heated to 40 °C. The COS (g) formed was directed to the 2-propanol/H2O solution of potassium isopropoxide using a cannula. After stirring at ambient temperature for 2 h, 200 mL of *n*-hexane was added to the reaction flask and the mixture stirred in an ice bath for 1 h. The salt was isolated as a white solid by vacuum filtration and washed with 25 mL of hexane and 10 mL of diethyl ether before drying in vacuo (10.69 g, 0.0688 mol, 21% yield - based on KOH). ¹H NMR (400 MHz, D_2O) δ (ppm) 1.14 (d, CH₃, 6H), 4.77 (q, O-CH-C, 1H). ¹³C NMR (400 MHz, D₂O) δ (ppm) 185.02, 70.33, 21.18. FTIR: (cm⁻¹) 1585 (C=O), 1127 (C-O), 1073 (C-S).

Solution Synthesis of $[Cu{SC(O)OCH(CH_3)_2}]_{16}$ ·2THF (1). To a 250 mL round-bottom flask were added [Cu(CH₃CN)₄](PF₆) (0.235 g, 0.63 mmol) and K[SC(O)OⁱPr] (0.100 g, 0.63 mmol) in a 100 mL THF solution. The reaction mixture was stirred at room temperature for 1 h. After 1 h, the reaction mixture was evaporated to dryness under vacuum. The crude yellow powder was washed thoroughly with deionized water (20 mL \times 5) and extracted with CH₂Cl₂ (10 mL \times 5). The resulting CH_2Cl_2 extract on evaporation yielded a pale yellow powder. Yellow crystals of (1) were obtained by diffusion of hexane into THF solution after 10 days. Yield 0.97 g (80%). Mp. 120-122 °C. ¹H NMR (300 MHz, d₆-(CD₃)₂CO): 1.28 (d,96H, CH₃), 1.78 (br, 8H, CH₂), 3.61 (br, 8H, CH₂) 4.94 (br, 16H, CH) ppm; FTIR data in KBr pellet (cm⁻¹): 681, 841, 911, 1088, 1179, 1332, 1373, 1466, 1614, 1702, 2880, 2937, 2980, 3475; Anal. Calcd (%) for C72H128O34S16Cu16: C, 28.19; H, 4.21; S, 16.72. Found: C, 28.12; H, 3.89; S, 16.97.

Solution Synthesis of $[Cu{SC(O)OCH(CH_3)_2]]_{96}$ (2). The synthetic procedure and stoichiometric amounts of reactants used for 2 are similar to those of 1. The only modification in the procedure was that

the experiment was carried out in acetone solvent (100 mL). Yellow crystals of (2) suitable for X-ray diffraction analysis were obtained by diffusion of hexane into acetone solution within a week. Yield 0.99 g (85%). Mp. 138–140 °C. ¹H NMR (300 MHz, d_6 -(CD₃)₂CO): 1.28 (d, 576H, CH₃), 4.95 (m, 96H, CH) ppm; FTIR data in KBr pellet (cm⁻¹): 677, 808, 840, 911, 1088, 1175, 1332, 1373, 1466, 1618, 1702, 2879, 2936, 2979, 3387; Anal. Calcd (%) for C₃₈₄H₆₇₂O₁₉₂S₉₆Cu₉₆: C, 26.29; H, 3.86; S, 17.55. Found: C, 26.39; H. 3.83; S, 17.38.

Synthesis of [Cu{SC(O)OCH(CH₃)₂]₉₆ (2) via a Solventless Route and Recrystallization in Acetone. Solid potassium O-isopropylmonothiocarbonate (100 mg, 0.632 mmol) was added to [Cu- $(CH_3CN)_4]PF_6$ (236 mg, 0.632 mmol) (molar ratio 1:1) in a clean dry mortar, and the solids were gently mixed. The reactants were ground together with a pestle for about 2-3 min until a homogeneous yellow paste formed. The paste is caused by the release of the free acetonitrile (liquid) and has a distinctive smell. The yellow paste was left in the mortar in a low heat oven (<50 °C) overnight to evaporate the CH₃CN off and allow the paste to dry. The resulting yellow solid was dissolved in acetone (10 mL), filtered over a plug of Celite to remove KPF₆ salt, and concentrated under reduced pressure. The light-yellow solid was recrystallized from acetone, and subsequent characterization of the material, including a single-crystal X-ray study, revealed it was identical to the solution formation of $[Cu{SC(O)} OCH(CH_3)_2\}]_{96}$ (2).

4.3. Crystallography. Reflections were collected on a Bruker APEXII CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystals were mounted on the tip of glass fibers with epoxy resin. Data reduction was performed with SAINT-Plus.⁵⁵ Absorption corrections for the area detector were performed by using the SADABS program.⁵⁶ Structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 by using the SHELXL package⁵⁷ incorporated in SHELXTL/PC V6.14 software^{57,58} in OLEX2.⁵⁹ The data collections for crystals of 1 and 2 were performed at 150(2) and 298(2) K, respectively. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained in geometrical positions to their parent atoms. The disordered solvated atoms located at the packing cavities of 1 and 2 were treated as a diffuse contribution to the overall scattering without specific atoms position by SQUEEZE/PLATON. Illustrations of some crystal structures were generated in Mercury⁶⁰ using POV-Ray. Crystallographic data of 1 and 2 are listed in Table S1.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00871.

Details regarding instrumentation and characterization; including UV–vis, ESI-MS, NMR, and X-ray crystallog-raphy; supporting Figures S1–S14 and Tables S1–S2(PDF)

Accession Codes

CCDC 1495899, 2068968, and 926958 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

A.K.G., J.-Y.C., and P.V.V.N.K. conceptualized the experiments. A.K.G. the synthesis of (1, 2), and J.-Y.C. the synthesis of (2). Characterizations were done by A.K.G., P.V.V.N.K., and J.-Y.C. A.K.G. and J.H.-L. performed the X-ray studies. W.D. was supervised by W.E.v.Z. and performed the solid-state reaction and characterization of (2) including verification of the similarity of the solution-based X-ray structure. P.V.V.N.K., W.E.v.Z., and C.W.L. wrote the original manuscript. C.W.L. and W.E.v.Z. supervised the project. All authors proofread, commented on, and approved the final manuscript for submission.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful for the financial support from the Ministry of Science and Technology Taiwan (MOST 109-2113-M-259-008) and for the research supported in part by the National Research Foundation of South Africa (Grant Number: 132014)

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