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Guest-induced Assembly of Bis(thiosemicarbazonato) Zinc(II) Coordination Nanotubes

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Abstract: A Zn^{II} complex of the dianionic tetradentate ligand formed by deprotonation of glyoxal-*bis*(4-phenyl-3-thiosemicarbazone) (H_2gtsp) is a [3 + 3] trinuclear triangular prism. Recrystallization of this complex in the presence of either of CO_2, CS_2 or CH_3CN leads to the formation of [4 + 4] open-ended charge neutral tetranuclear coordination nanotubes, approximately 2 nm in length and with internal dimensions large enough to accommodate linear guest molecules, which serve to template their formation. Upon removal of the templating molecules the nanotubes demonstrated reversible sorption of CO_2 with an isosteric enthalpy of sorption of 28 kJ mol^{-1} at low loading.

The directional and reversible nature of coordinate bonds permits supramolecular transformations as functions of specific stimuli such as solvent, concentration, counterion or guest.[1] Template molecules serving as guests within a cavity can induce product formation and stabilization in what has been termed "guest-induced assembly."[2] Guest molecules can also shift the equilibrium from the self-assembled product to an otherwise entropically unfavorable product.[3] The host-guest chemistry of 'nanotubes' with one dimensional hollow channels has potential for applications in molecular separation, gas sorption and storage or as reaction vessels.[4] Despite the abundance of supramolecular coordination architectures achieved in recent years,[5] reports of discrete coordination nanotubes of finite length are relatively limited.[6] Pioneering work focused on templated nanotubes consisting of oligo(pyridine) linkers and [*cis*-Pd^{2+}(en)] (en = ethylenediamine),[7] and semi-rigid ligands with Hg(II).[8]

The rotational flexibility demonstrated by thiosemicarbazone (tsc) and *bis*(thiosemicarbazone) (btsc) ligands allows them to exist in different configurations either as monodentate or polydentate ligands and with multiple binding modes that can lead to diverse and elaborate supramolecular structures from identical metal-ligand combinations.[9] Zn(btsc) complexes have been isolated in both tetrahedral or square pyramidal geometries where the ligand functions as a dianionic N_2S_2 donor.[10] The fifth coordination site is usually occupied by a monodentate donor such as a solvent molecule or atom from a neighboring complex.[10b, 11] Several Zn(btsc) complexes display fluorescence and chromophoric properties that have been utilized to track their cellular uptake and distribution in live cells and to estimate the binding affinities of metal-transporting proteins.[12] Zn(btsc) complexes have also been investigated as potential catalysts in cyclic carbonate synthesis and H_2 evolution and oxidation.[13]

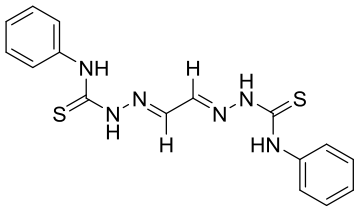

Figure 1. The structure of glyoxal-*bis*(4-phenylthiosemicarbazone), H_2gtsp.

As part of an exploratory study of the supramolecular chemistry of Zn(btsc) complexes we prepared the Zn^{II} complex of glyoxal-*bis*(4-phenylthiosemicarbazone) (H_2gtsp) (Figure 1). Solid-state and solution fluorescence emission analysis of the bright red/orange solid showed an emission maximum at λ_{em} = 569 nm, λ_{ex} = 484 nm (Supporting Information, Figure S2). Crystals suitable for single crystal X-ray diffraction were grown from a concentrated solution in dimethylsulfoxide (DMSO). The red crystals revealed a neutral triple-helical trinuclear complex, [Zn_3(gtsp)$_3$] (Figure 2), structurally similar to the recently published Zn^{II} complex of glyoxal-*bis*(4-methyl-4-phenyl-thiosemicarbazone) (H_2gtsc).[12d] The discrete complex has D_3 point group symmetry and consists of three identical Zn^{II} cations in distorted tetrahedral N_2S_2 geometries. The ligand is in an s-*trans* configuration about the C(8)-C(8)′ backbone bond and a *cis* configuration about the C(7)-N(2) partial double bond, which allows each ligand to coordinate two Zn^{II} cations. Edge-to-face interactions involving the phenyl groups may be assisting in the self-cyclization. The H-to-ring centroid distance is 2.9 Å (cf. 2.5 – 2.7 Å for the benzene dimer). The complex is chiral and both left-handed (Λ) and right-handed (Δ) helical complexes are present in a single crystal to give an overall racemic mixture. The disordered DMSO molecules could not be satisfactorily modelled and thus the SQUEEZE algorithm (*PLATON*)[14] was employed to treat the disordered solvent. On the basis of the solvent volume calculations the formula of the solvated complex was estimated to be [Zn_3(gtsp)$_3$]·12DMSO.

Analysis of a solution of the Zn^{II} complex by electrospray mass spectrometry indicated the presence of a dominant peak for the monomeric species (*m/z* = 419.01) but also significant quantities of the dimeric (*m/z* = 841.01), trimeric species (*m/z* = 1259.01) and even a tetrameric species (*m/z* = 1681.01) (Supporting Information, Figure S3).[15]

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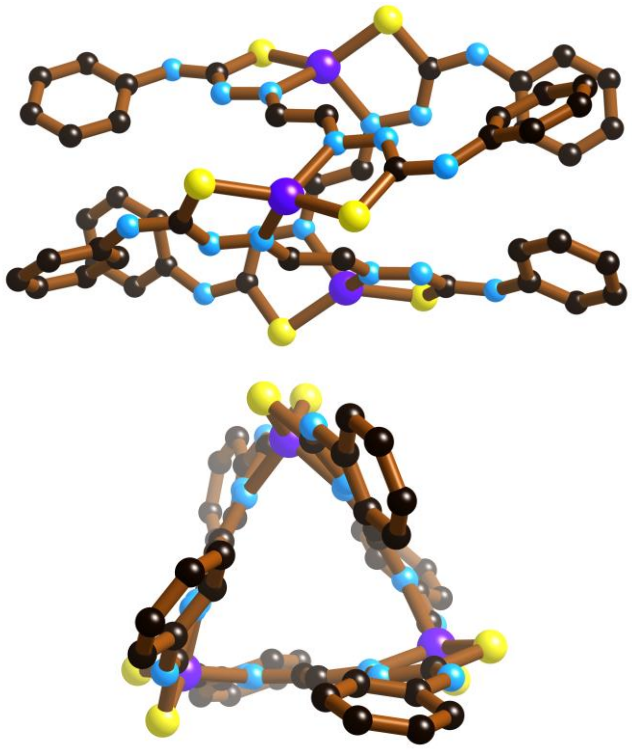

Figure 2. Representations of the trinuclear $[Zn_3(gtsp)_3]\cdot 12DMSO$ complex (solvent omitted for clarity).

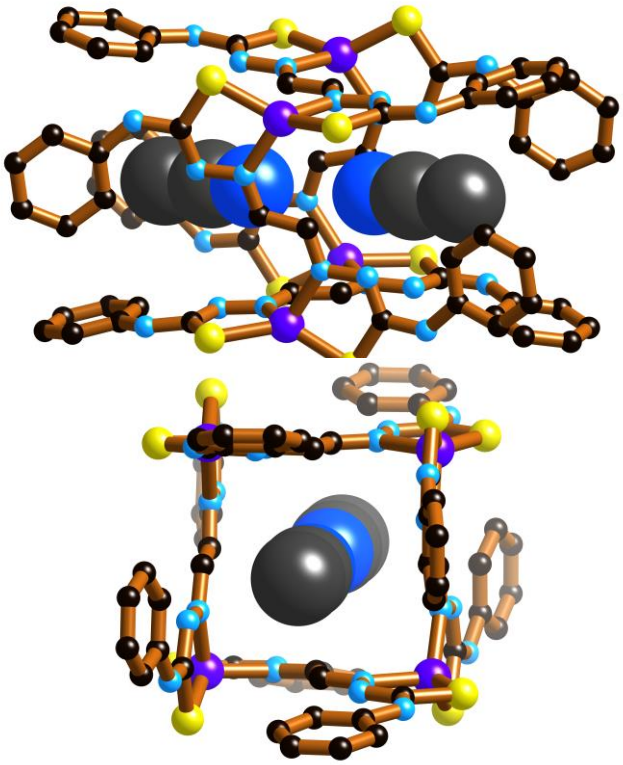

Figure 3. Representations of the $[Zn_4(gtsp)_4 \supset 2CH_3CN]$ nanotube with two guest molecules of CH_3CN, which are shown in a space-filling mode (DMSO omitted for clarity).

Given the formation of $[Zn_3(gtsp)_3]$ it was thought that the tetrameric species identified in the mass spectrum may be a complex in which four ligands and four Zn^{II} centres combine to form the tetranuclear complex $[Zn_4(gtsp)_4]$. The coordination geometries of the Zn^{II} cations in $[Zn_3(gtsp)_3]$ are significantly distorted from an ideal tetrahedral geometry and it was expected that the formation of a larger complex would reduce the strain and result in a coordination geometry that is preferred on an enthalpic basis. Entropy, on the other hand, is likely to favor formation of $[Zn_3(gtsp)_3]$ given that it is assembled from a smaller number of components.[5a]

The intriguing presence of the tetrameric species in the electrospray mass spectrum prompted us to explore a template strategy that might lead to its isolation. We chose the approximately linear acetonitrile (CH_3CN) as a templating guest. The Zn(gtsp) powder was dissolved in DMSO and then CH_3CN was added. Vapor diffusion of diethyl ether into the mixture in a sealed vessel yielded single crystals suitable for X-ray diffraction analysis that revealed the formation of $[Zn_4(gtsp)_4]$ with inclusion of two CH_3CN molecules within the square channel of a nanotube characterized by a square arrangement of Zn^{II} cations encapsulated by the dianionic ligands (Figure 3). Although a previously reported Zn^{II} complex of a tsc ligand was reported as a tetranuclear array of Zn^{II} atoms on the vertices of a square parallelogram,[16] to the best of our knowledge this is the first example of the formation of an inclusion complex.

The discrete complex $[Zn_4(gtsp)_4]$ consists of four identical Zn^{II} cations each in a distorted tetrahedral N_2S_2 geometry. The Zn^{II} cations are again coordinated to two doubly deprotonated ligands resulting in two 5-membered chelate rings and the angle between the planes defined by the chelate rings of ~88°; the corresponding angle in $[Zn_3(gtsp)_3]$ is ~78°, which is consistent with a higher level of strain in the latter. The distance between the Zn^{II} cations, which are located at the corners of a square is 6.187 Å, which is slightly longer than the corresponding separation of 6.157 Å for $[Zn_3(gtsp)_3]$. The four ligands of the $[Zn_4(gtsp)_4]$ form the walls of a tube that is approximately 19.3 Å (van der Waals surface to surface), similar to that of $[Zn_3(gtsp)_3]$. Although the channel has a square cross-section, the width of the channel (defined by the separation between van der Waals surfaces) varies from 3.0 Å at the mid-point of the channel to 5.0 Å at the ends. This is presumably a consequence of the orientation of the CH_3CN molecules with the nitrogen atoms pointing toward each other. The sterically demanding methyl group of the CH_3CN causes the phenyl groups to splay out. As with $[Zn_3(gtsp)_3]$ both enantiomeric forms of $[Zn_4(gtsp)_4]$ are present in the crystal. Parallel complexes, of the same handedness, form layers with the internal channels of the tubes oriented perpendicular to the plane of the layer (Figure 4). Adjacent parallel layers contain complexes with the opposite handedness and as such stack in an A(Δ) B(Λ) A(Δ) B(Λ)... manner.

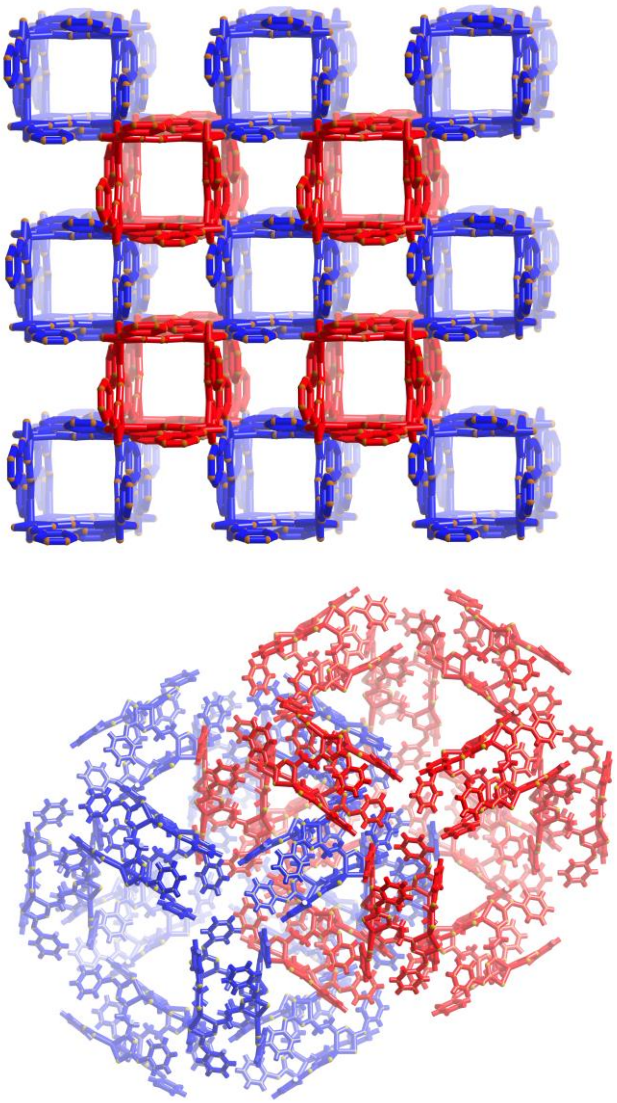

Figure 4. Top: The packing arrangement for the tetragonal structure of $[Zn_4(gtsp)_4 \supset 2CH_3CN]\cdot DMSO$. Red nanotubes are the opposite handedness to the blue nanotubes, which stack in an A(Δ) B(Λ) A(Δ) B(Λ)... manner. Bottom: The packing arrangement for the cubic structure of $[Zn_4(gtsp)_4 \supset 2CH_3CN]\cdot DMF$. The twelve blue nanotubes shown are aligned along the edges of a cube with dimensions equal to that of the unit cell. The cube belongs to a 3D primitive cubic network. The red nanotubes are of the opposite handedness and belong to a second interpenetrating primitive cubic network.

The nanotube is also formed when DMF/CH_3CN is used as the solvent with CH_3CN in the square channels but with a remarkably different packing arrangement (Figure 4). In these crystals, the four-fold axes that run along the channels of six tubes converge upon a point that may be considered as a 6-connecting node within a simple cubic network. Within the network the tubes are of the same handedness. This packing arrangement leaves large cubic holes which are occupied by a symmetry-related interpenetrating network containing complexes of the opposite handedness.

The successful formation of the tubes prompted an investigation of other suitably sized molecules that may serve as templates. Carbon dioxide and carbon disulfide seemed appropriate candidates based on their size and shape. The introduction of CO_2, in the form of dry ice, into the reaction mixture along with DMF did indeed lead to the selective crystallization of an essentially isostructural species demonstrating that the linear CO_2 molecule can play the crucial role of template. Fourier difference maps indicated electron density within the channels consistent with a pair of disordered CO_2 molecules. Similar results were obtained with DMF/CS_2.

There is currently great interest in porous materials that can selectively adsorb CO_2.[17] Coordination nanotubes have shown promising adsorption properties,[18] including a study that investigated the CO_2 and CH_4 adsorption properties of porous ditriazole coordination nanotubes as a function of pore size.[19] The complementary host-guest relationship existing within $[Zn_4(gtsp)_4 \supset 2CH_3CN]$ prompted an investigation as to whether the removal of CH_3CN from the channel would generate a porous material capable of adsorbing CO_2 from the gas phase.[20] Thermogravimetric analysis showed that the solvent (CH_3CN and DMF) could be removed completely by heating the crystals to 178 °C, resulting in a 10% weight loss (Supporting Information, Figure S4). Prior to gas-sorption studies, the crystalline solid was desolvated under vacuum at 200 °C for 3 h. The adsorption of CO_2 was measured at 258, 273 and 298 K (Supporting Information, S5). Carbon dioxide sorption data were collected up to 30 atm at 298 and 273 K, and 18 atm at 258 K. The CO_2 isotherms showed sorption behavior similar to a material with reversible type I adsorption character.[21] At 298 K and 1 atm, approximately 0.8 molecules of CO_2 are adsorbed per nanotube (Figure 5). At pressures above 5 atm, the isotherm plateaus with approximately 2.6 molecules of CO_2 per nanotube at 298 K and 30 atm. The quantity of CO_2 adsorbed is in reasonable agreement with the amount expected from the crystal structure determinations. The adsorption of slightly more than two CO_2 molecules per complex may be a consequence of an external association between host and guest. For comparative purposes, CO_2 adsorption by the desolvated

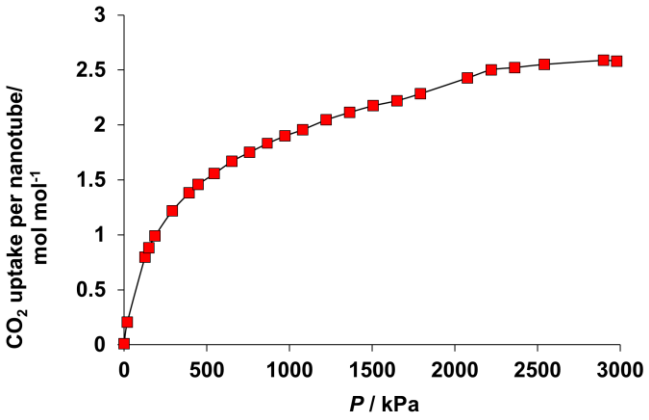

Figure 5. CO_2 sorption isotherm measured on a desolvated sample of $[Zn_4(gtsp)_4]$ nanotubes at 298 K.

trinuclear species, which possesses an internal channel that would only be able to accommodate a sphere of 0.9 Å diameter, indicated a maximum uptake of only 0.1 molecules of CO_2 per complex (Supporting Information, Figure S6). It would seem likely that this adsorption reflects the uptake into intermolecular voids of the desolvated material.

The CO_2 isotherms obtained at 273 and 258 K were utilized to calculate a 28 kJ mol^{-1} isosteric enthalpy of sorption at low loading, a value that decreased marginally as the loading increased (Supporting Information, Figure S7).[22] Such a value indicates a significant interaction between host and guest and is consistent with size complementarity between CO_2 and the $[Zn_4(gtsp)_4]$ nanotube cavity.

In summary, the btsc ligand H_2gtsp served as a flexible dianionic bridging ligand to self-assemble with Zn^{II} to form trinuclear [3 + 3] triangular prisms. The introduction of templating molecules leads to the formation of charge neutral tetranuclear [4 + 4] square nanotubes featuring 4 Zn^{II} cations and 4 bridging ligands, where the templating agent is included as a guest. The template can be readily removed from the inclusion complex while maintaining a porous material capable of adsorbing upwards of 2 molecules of CO_2 per nanotube with an initial isosteric binding enthalpy of approximately 28 kJ mol^{-1}.

Acknowledgements

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Keywords: coordination nanotube, guest-induced assembly, thiosemicarbazone, zinc

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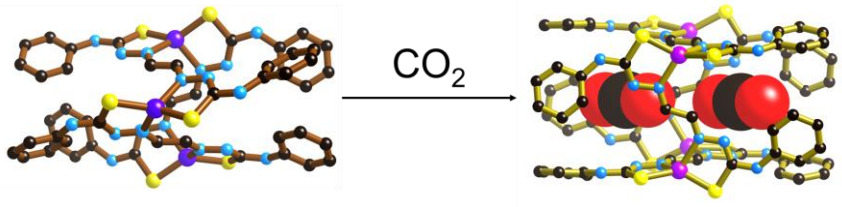

B. M. Paterson, K F. White, J M. White, B. F. Abrahams* and P. S. Donnelly**

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Flexible dianionic bridging ligands are used to form charge neutral triangular prisms with three inorganic zinc(II) centres. Synthesis in the presence of linear templating molecules, CO_2, CS_2 and CH_3CN, leads to the formation of charge neutral square coordination nanotubes featuring four zinc(II) centres with the templating agent included as a guest. The template can be removed from the inclusion complex while maintaining a porous material capable of adsorbing upwards of 2 molecules of CO_2 per nanotube.