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A Supramolecular Synthon for H-Bonded Transition Metal Arrays

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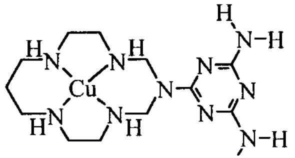
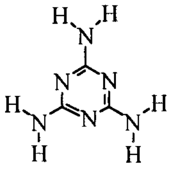
The heterocycle melamine appended to a 14-membered polyazamacrocyclic copper(II) complex ring exhibits a strong propensity for ordered arrays driven by H-bonding forces. In this work, the X-ray crystal structures of three distinctly different arrays based on the same macrocyclic complex are reported, comprising cocrystals with barbituric acid (a sheet structure) and cyanuric acid (a linear chain) and the parent complex (a linear tape).

The rational self-assembly of ordered supramolecular arrays in the solid state using noncovalent forces such as hydrogen bonding[1−4] and $\pi-\pi$ stacking[5] is a rapidly expanding field. Cooperative intermolecular interactions that may be encouraged through alignment of molecules in particular ways in the solid state can result in novel magnetic,[6] conductive,[7] and nonlinear optical[8] properties. In addition, there are a rapidly growing number of noncovalently linked 3-D crystalline host lattices that are sufficiently robust to be able to reversibly form clathrates with small guest molecules.[9,10] Although it is a field in its own right, molecular recognition in solution[11−16] is driven by noncovalent forces, and our understanding of intermolecular interactions has been greatly assisted through solid state crystallographic characterization of supramolecular assemblies.

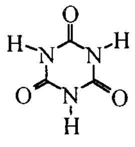
For any new compound, the unpredictability of its crystal structure (as opposed to its molecular structure) is the greatest problem confronting those wishing to assemble molecules into designer-made crystalline arrays.[17] In the absence of "information" being encoded into molecules so that they will assemble in a certain way, there can be little hope that genuinely predictable assemblies can arise from the innumerable possibilities available to a molecule across all 3-D space groups. If one wishes to develop noncovalently linked crystalline arrays for the purpose of their magnetic or conductive properties, then transition metal ions naturally offer a wide choice of stable and readily available building blocks that can convey the desired paramagnetism (or ferromagnetism) to the bulk material. The H-bond is the best understood and probably most predictable noncovalent intermolecular force. Traditionally, organic chemistry[18] has been the domain of crystal engineering through H-bonding interactions, but transition metal coordination chemistry can also exploit H-bonding if prudent ligand design is practiced. Our approach has been to employ strongly H-bonding organic components that are tethered to macrocyclic transition metal complexes, and allow these organic H-bonding fragments to direct the assembly of the complex ions in the solid state. The coordination environment of the metal is constrained by the cyclic ligand, so the metal may be considered to be an inert substituent on the H-bonding organic fragment. We recently reported[19] the synthesis of the new melamine appended azamacrocyclic Cu^{II} complex $[CuL]^{2+}$ and the crystal structure of its protonated analogue $[Cu(HL)](ClO_4)_3$. A feature of this structure was the assembly into chains of macrocycles linked by H-bonds involving the melamine amino groups and bridging water molecules. Given the propensity for ordering in the system, we have now investigated the cocrystallization of $[CuL]^{2+}$ with the strongly H-bonding organic molecules cyanuric acid (CA) and barbituric acid (BA). Both of these heterocycles have featured prominently in studies of self-assembled H-bonded arrays in organic chemistry,[20] yet few examples of their employment as supramolecular synthons in transition metal chemistry are known. One of the goals of this investigation was to investigate the influence that competing H-bonding guests have on the assembly of ordered arrays of $[CuL]^{2+}$ ions in the solid state.



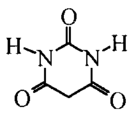
$[CuL]^{2+}$



melamine



CA



BA

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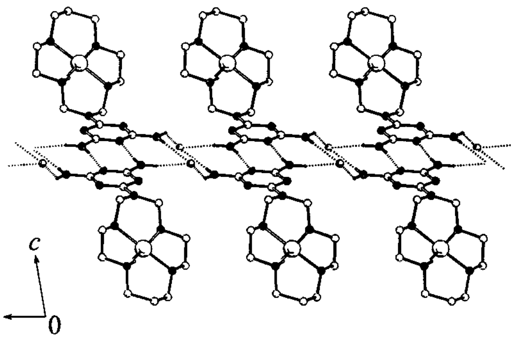

Figure 1. View of the $[CuL](ClO_4)_2{\cdot}H_2O$ ribbon structure (ClO_4^- anions, alkyl and water H atoms omitted for clarity, N atoms are shaded). Selected bond lengths (Å): Cu−N 2.009(7)−2.026(6); C−N (triazine) 1.31(1)−1.34(1), (amino) 1.338(9)−1.375(9).

To this end we have identified a variety of 1-D arrays derived from intermolecular H-bonding interactions involving the pendent melamine group of $[CuL]^{2+}$ in a central role.[21]

The crystal structure[22] of $[CuL](ClO_4)_2{\cdot}H_2O$ reveals the assembly of buckled H-bonded ribbons (Figure 1). The two strands of the ribbon are linked by a pair of centrosymmetrically related H-bonds between the triazine N atom para to the macrocyclic substituent and an amino H-atom ($R^2_2(8)$ motif).[23] This centrosymmetric dimer formation is reminiscent of the crystal structures of melamine and some of its protonated analogues.[24,25] In the present structure, a water molecule cross-links the two strands ($R^2_4(8)$) as well as providing a bridge between adjacent macrocyclic units. The coordination environment of the metal ion is not significantly different from that identified for the protonated analogue $[Cu(HL)](ClO_4)_3$.[19]

Cocrystallization of $[CuL]^{2+}$ with BA gave a zwitterionic adduct involving proton transfer from the acid to the complex cation.[26] Inspection of the respective protonation constants of BA (pK_a 4.0)[27] and $[CuL]^{2+}$ (pK_a 4.2)[19] explains this observation. The structure of this adduct $[Cu(HL)][BA\text{-}H](ClO_4)_2{\cdot}3H_2O$ is shown in Figure 2, and it is apparent that the complementary DAD:ADA interaction generally formed between melamine and barbituric acids has been prevented by protonation of the pendent melamine group. Instead, centrosymmetric H-bonded barbiturate dimers result, which straddle adjacent chains of macrocycles through H-bonding interactions between the barbiturate O atoms and the melamine amino H atoms. This array is comparable with that found for $[Cu(HL)](ClO_4)_3$ where an H_2O-linked ribbon structure was identified.[19] In the present case, a water molecule is H-bonded with the central melaminium proton (instead of ClO_4^- found in the structure of $[Cu(HL)](ClO_4)_3$), while the adjacent O atoms of the bridging barbiturate anion occupy the remaining H-bond acceptor sites at the DDD face of the pendent group. The (intra-ring) C−C bond lengths in the barbiturate anion (1.35(2) and 1.39(2) Å) are comparable with those found in crystal structures of other C-deprotonated barbiturate anions such as potassium 5-ethylbarbiturate (1.396(5) Å).[28] Moreover, these bond lengths are significantly shorter than those identified in the crystal structures of BA (1.498(5) Å)[29] and N-deprotonated barbiturates such as sodium barbital

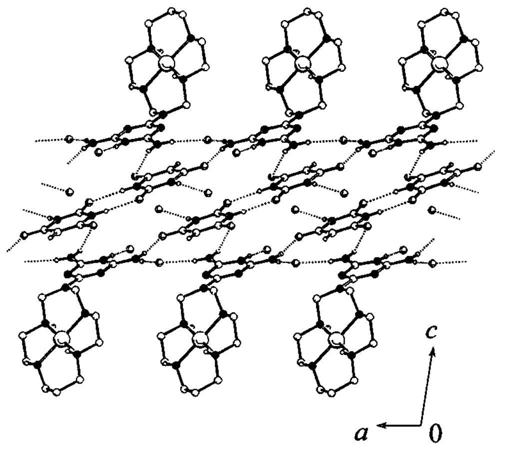

Figure 2. View of the $[Cu(HL)][BA\text{-}H](ClO_4)_2{\cdot}3H_2O$ cocrystal ribbon structure (ClO_4^- anions, alkyl and water H atoms omitted for clarity, N atoms are shaded). Selected bond lengths (Å): Cu−N 2.00(1)−2.04(1); C−N (triazine) 1.31(2)−1.35(2), (amino) 1.28(2)−1.37(2), (barbiturate) 1.32(2)−1.42(2); C−O 1.23(2)−1.27(2).

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[21] Crystals of each complex were grown by vapor diffusion of EtOH into neutral aqueous solutions (3 mL) of $[CuL](ClO_4)_2$ (40 mg)[19] and the corresponding organic acid (10 mg), or without any added acid in the case of $[CuL](ClO_4)_2{\cdot}H_2O$.

[22] Crystal data for $[CuL](ClO_4)_2{\cdot}H_2O$: $C_{12}H_{28}Cl_2CuN_{10}O_9$, $M_r = 590.88$, pink prism (0.6 × 0.3 × 0.1 mm), triclinic, space group $P\bar{1}$ (No. 2), $a = 8.2294(8)$ Å, $b = 8.557(1)$ Å, $c = 18.683(3)$ Å, ($\alpha = 79.45(1)°$, $\beta = 83.55(1)°$, $\gamma = 72.79(1)°$, $V = 1243.6(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.578$ g cm^{-3}, $F(000) = 610$, μ(Mo Kα) = 11.55 cm^{-1}. Of 4686 measured reflections, 4356 were unique; $R_{int} = 0.0276$ ($2.2° < \theta < 25°$, $\omega-2\theta$ scan, $T = 293$ K, Mo Kα radiation, graphite monochromator, $\lambda = 0.710\,73$ Å). Data for each structure was collected on an Enraf-Nonius CAD4 diffractometer. Absorption correction was performed (ψ-scans) using XTAL3.2 ($T_{min,max} = 0.763$, 1.000). The structure was solved by Patterson methods with SHELXS86 and refined by full-matrix least squares on F^2 with SHELXL-93. Views of all structures were generated with the PLUTON program. All non-H atoms were refined with anisotropic thermal parameters except perchlorate O atoms attached to Cl(2) which were equally disordered over two positions. H atoms for the water molecule were located from difference maps whereas all other H atoms were included at estimated positions. At convergence R1 = 0.0893 for 2687 observed reflections ($F > 2\sigma(F)$) and wR2 = 0.2597 where $w^{-1} = (\sigma^2(F_o^2) + (0.1768P)^2 + 3.06P)$, goodness of fit = 1.083 for 304 parameters, residual extrema +1.4 and −0.9 e Å^{-3}. Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre (deposition no. CCDC 110261). Copies of this data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax, int code +(1223)336-033; E-mail, deposit@chemcrys.cam.ac.uk).

[23] For a full definition of these symbols, see: Etter, M. C.; MacDonald, J. C.; Bernstein, J. *Acta Crystallogr., Sect. B* **1990**, *46*, 256. Briefly, R = ring; sub- and superscripts = number of H-bond acceptors and donors, respectively; numeral in brackets refers to size of the ring.

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[26] Crystal data for $[Cu(HL)][BA\text{-}H](ClO_4)_2{\cdot}3H_2O$: $C_{16}H_{36}Cl_2CuN_{12}O_{14}$, $M_r = 655.54$, pink needle (0.5 × 0.13 × 0.1 mm), triclinic, space group $P\bar{1}$ (No. 2), $a = 8.436(2)$ Å, $b = 8.439(2)$ Å, $c = 22.997(8)$ Å, $\alpha = 97.85(3)°$, $\beta = 91.82(2)°$, $\gamma = 111.40(2)°$, $V = 1504.1(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.667$ g cm^{-3}, $F(000) = 782$, μ(MO Kα) = 9.88 cm^{-1}. Of 5779 measured reflections, 5263 were unique; $R_{int} = 0.1237$ ($1.8° < \theta < 25°$, $\omega-2\theta$ scan, $T = 293$ K, Mo Kα radiation, graphite monochromator, $\lambda = 0.710\,73$ Å). Satisfactory empirical absorption correction (ψ-scans) could not be applied so the data did suffer as a consequence (peaks of ca. 1 e A^{-3} surrounding the Cu atom). The structure was solved by Patterson methods with SHELXS86 and refined by full-matrix least squares on F^2 with SHELXL-93. All non-H atoms were refined with anisotropic thermal parameters except minor contributors to perchlorate disorder. Water and barbiturate H atoms were located from difference maps whereas all other H atoms were included at estimated positions. At convergence R1 = 0.1192 for 1821 observed reflections ($F > 2\sigma(F)$) and wR2 = 0.2873 where $w^{-1} = (\sigma^2(F_o^2) + (0.2040P)^2 + 2.42P)$, goodness of fit = 1.032 for 420 parameters, residual extrema +1.0 and −1.5 e Å^{-3} (deposition no. CCDC 110262).

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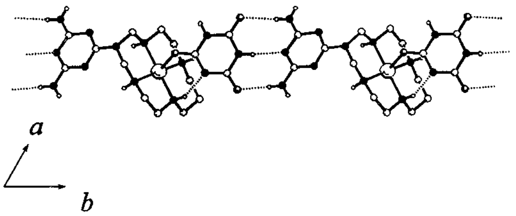

Figure 3. View of the [CuL][CA-H](ClO_4)•$3H_2O$ chain structure (one chain shown only, $C1O_4^-$ anions, alkyl and water H atoms omitted for clarity, N atoms are shaded). Selected bond lengths (Å): Cu−N 2.006(6)−2.039(6); C−N (triazine) 1.317(8)−1.361(8), (amino) 1.323(9)−1.381(8), (cyanurate) 1.338(9)−1.388(9); C−O 1.219(8)−1.251(8).

(sodium 5,5-diethyl barbiturate, 1.524(3) Å),[30] where typical C−C single bonds were identified. There is an organic analogue of the present crystal structure in the melaminium:barbiturate ($[HMel]^+$:$[BA\text{-}H]^-$) cocrystal[31] where a zwitterionic H-bonded adduct was found. However, in this case, steric effects of the attached macrocyclic ring in $[CuL]^{2+}$ direct multiple H-bonding partners to approach the melamine ring from the edge opposite from the macrocyclic substituent. Therefore, unlike the structure of ($[HMel]^+$:$[BA\text{-}H]^-$), there are no other DAD sites available for the barbiturate anion to bind once the melamine residue of the complex is protonated. Cocrystallization of melamine derivatives with weaker acids such as barbital (pK_a 8.0)[27] do not result in proton transfer,[32] and we anticipate that cocrystallization of barbital with $[CuL]^{2+}$ will result in discrete pairs of complex cations and barbital molecules linked via a triply H-bonded bridge.

The crystal structure[33] of [CuL][CA-H](ClO_4)•$3H_2O$ identified l-D chains of complex cations and cyanurate anions. The links in the chain comprise (i) a triply H-bonding interaction between the melamine (DAD) and cyanurate (ADA) fragments (R^3_3-(12))[23] and (ii) a coordinate bond between Cu and a cyanurate O atom. There are two crystallographically independent (but effectively identical) chains both running parallel with the *b* axis, and one of these is shown in Figure 3. By comparison with BA, the weaker acid CA (pK_a 6.8)[34] cannot protonate $[CuL]^{2+}$ and the complementary (O:H:O•••H:N:H) H-bonding motif is not disturbed at neutral pH. The site of deprotonation on the cyanurate anion was identified unambiguously during refinement, and this is seen clearly in Figure 3, where an intramolecular H-bond with one secondary amine H atom is observed, which skews the conformation of the coordinated cyanurate anion. There is no significant difference between the three C−O bond lengths in either independent cyanurate anion, or between the C−N bonds in the ring, indicating that the negative charge is delocalized. Water molecules do not disrupt the chains to any significant extent and are mainly associated with each other in H-bonding. A recent survey of crystallographic structures containing cyclic H-bonding interactions found that this same triply bonded O:H:O•••H:N:H interaction has been observed in 97% of structures where these two functionalities are present,[35] and this high probability has been exploited in an effort to arrive at predictable supramolecular structures. We believe that the structure of [CuL][CA-H](ClO_4)•$3H_2O$ is the first crystallographically characterized example of this H-bonding motif in a transition metal complex. Deprotonation enhances the nucleophilicity of the O atoms on the cyanurate anion, and coordinate bond formation is the result. This feature gives an added dimension to H-bonded arrays comprising transition metals. Indeed crystal engineering of transition metal arrays through intermolecular coordinate bond formation is a field of considerable current interest,[36] but the coupling of H-bonding and coordinate bond formation in a rational way to generate arrays of transition metal ions is an approach still in its infancy.[37]

We have now identified H-bonded arrays comprising the $[CuL]^{2+}$ (or $[Cu(HL)]^{3+}$) adducts with perchlorate,[19] barbiturate, and cyanurate and also in the absence of any coprecipitant. The DAD motif of $[CuL]^{2+}$ has been shown to be a potent H-bonding supramolecular synthon. In the absence of H-bonding competitors, the melamine unit will recognize itself, to form ribbons connected by centrosymmetric 8-membered H-bonded rings. If the complementary triply H-bonding cyanurate anion is present, a 1-D array results comprising alternating H-bonded and coordinate bonded links between complex units. Upon protonation, the H-bonding motif of $[Cu(HL)]^{3+}$ is transformed into a DDD pattern, and recognition of H-bonding acceptors such as ClO_4^- and H_2O is promoted. An important point to emerge from these studies is that the metal ion plays a minor role in the formation of each supramolecular array. By contrast, H-bonding forces dictate the metal−metal distances and their relative orientations. We anticipate that other divalent metal ions (Ni^{II}, Zn^{II}, Pd^{II}) will be isostructural and the possibility for the self-assembly of heterometallic arrays and doped systems should be accessible. We are currently pursuing these goals.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Crystal data for [CuL][CA-H](ClO_4)•$3H_2O$: $C_{15}H_{34}ClCuN_{13}O_{10}$, M_r = 655.54, pink plate (0.2 × 0.2 × 0.03 mm), triclinic, space group $P\bar{1}$ (No. 2), a = 13.993(2) Å, b = 14.401(2) Å, c = 15.727(1) Å, α = 75.290(9)°, β = 65.41(1)°, γ = 69.677(9)°, V = 2680.1(6) Å^3, Z = 4, ρ_{calcd} = 1.625 g cm^{-3}, $F(000)$ = 1364, μ(Mo Kα) = 9.90 cm^{-1}. Of 9846 measured reflections, 9425 were unique; R_{int} = 0.0517 (1.5° < θ < 25°, ω−2θ scan, T = 293 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å). Absorption correction was performed (ψ-scans) using XTAL3.2 ($T_{min,max}$ = 0.852, 1.000). The structure was solved by Patterson methods with SHELXS86 and refined by full-matrix least squares on F^2 with SHELXL-93. All non-H atoms were refined with anisotropic thermal parameters except minor contributors to perchlorate disorder. Water and cyanurate H atoms were located from difference maps whereas all other H atoms were included at estimated positions. At convergence R1 = 0.0538 for 3888 observed reflections ($F > 2\sigma(F)$) and wR2 = 0.1216 where $w^{-1} = (\sigma^2(F_o^2) + (0.0642P)^2 + 2.42P)$, goodness of fit = 1.012 for 725 parameters, residual extrema +0.7 and −0.4 e Å^{-3} (deposition no. CCDC 110263).

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