dimethylcyclohexane and *cis*-2-heptene, and the significant incorporation of O_2 into the alcohol and epoxide products. Such catalytic behavior strongly resembles that of $[Fe^{II}(6\text{-}Me_3\text{-tpa})(CH_3CN)_2]^{2+}$ (**3**).[5–7] Perhaps even more compelling is the catalysis of *cis*-dihydroxylation by β-**1**. Not only are the *cis*-diol/epoxide ratios increased by six- to tenfold relative to those observed for α-**1**, but the cyclooctene *cis*-dihydroxylation product also derives both oxygen atoms from H_2O_2, as reported for **3**.[4, 6]

Our results show that the small change in ligand topology around the metal center between α-**1** and β-**1** elicits dramatically distinct outcomes in the hydrocarbon oxidation reactions observed for these two isomers, ones that parallel the contrasting behavior of **2** and **3**. The difference between **2** and **3** is less subtle; **3** has 6-Me substituents whose steric effects affect the spin state of the Fe^{III}–OOH intermediate,[15] which in turn influences the course of the oxidations (Scheme 2, right branch).[5–7] By analogy, we propose that the distinct ligand topologies of α-**1** and β-**1** give rise to different spin states for their respective Fe^{III}–OOH intermediates. That the α-ligand topology exerts a stronger crystal field is clearly manifested in ^1H NMR experiments on the Fe^{II} catalysts in CD_3CN. While both isomers exhibit large paramagnetic shifts at 25 °C indicative of high-spin metal centers (Figure 1), the α isomer undergoes a transition to a diamagnetic low-spin form as it is cooled to −45 °C, indicated by a spectrum that spans only 12 ppm. In contrast, the β isomer remains high spin at −45 °C.

In summary, ligand effects appear to play a significant role in determining the course of hydrocarbon oxidation by nonheme iron catalysts in combination with H_2O_2. One important factor is the availability of two *cis*-labile sites as demonstrated by Chen et al.[5, 6] in a comparison of related tetradentate and pentadentate ligands and by Mekmouche et al.[16] in a comparison of $[Fe(L)X_2]$ (X = Cl or CH_3CN) catalysts. We have also shown the dramatic effect of introducing 6-methyl substituents on pyridine ligands.[5–7] Herein, we show that the catalytic chemistry can be controlled by ligand topology. This work demonstrates that exquisite tuning of the reaction mechanisms can be accomplished by subtle control of the coordination environment of the nonheme iron site. Such fine tuning may also serve as a precedent to understand the diversity on the reactions of hydrocarbon oxidation catalyzed by nonheme iron enzymes.

Experimental Section

β-$[Fe^{II}(bpmcn)(CF_3SO_3)_2]$ (β-**1**) was prepared as previously described.[8]

α-$[Fe^{II}(bpmcn)(CF_3SO_3)_2]$ (α-**1**) was prepared from α-$[Fe^{II}(bpmcn)Cl_2]$. Overnight reaction of bpmcn (1.63 g, 5 mmol) in CH_3CN (7 mL) with a vigorously stirred suspension of $FeCl_2$ (0.64 g, 5 mmol) in CH_3CN (3 mL) afforded a yellow precipitate that was filtered, washed with CH_3CN and dried under vacuum to afford the product α-$[Fe^{II}(bpmcn)Cl_2]$ (1.97 g; 87 %). Elemental analysis calcd (%) for $C_{20}H_{28}Cl_2FeN_4 \cdot H_2O$: C 51.19, H 6.44, N 11.94; found: C 51.38, H 6.20, N 12.21. A suspension of α-$[Fe^{II}(bpmcn)Cl_2]$ (800 mg, 1.78 mmol) in CH_3CN (5 mL) was then treated with a solution of $AgCF_3SO_3$ (912 mg, 3.55 mmol) in CH_3CN (4 mL), resulting in the formation of a fine precipitate of AgCl, which was filtered away after allowing the mixture to stir. The filtrate was then dried in vacuo, yielding the desired complex as a pale yellow powder. Recrystallization from CH_2Cl_2/diethyl ether afforded α-**1** as large pale yellow blocks (1.19 g, 99 %). Elemental analysis calcd (%) for $C_{22}H_{28}F_6FeN_4O_6S_2$: C 38.95, H 4.16, N 8.26, S 9.45; found: C 38.97, H 4.37, N 8.30, S 9.41.

Received: January 16, 2002
Revised: March 19, 2002 [Z18530]

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Design of a Bilayer Structure in an Organic Inclusion Compound**

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Kenneth D. M. Harris*

Since their discovery over 50 years ago,[1, 2] several hundreds of urea inclusion compounds[3–11] have been prepared containing different types of guest molecules (mainly based on *n*-alkane chains, with only a limited degree of substitution allowed). The vast majority of urea inclusion compounds are based on a hexagonal host structure[3, 12] that comprises continuous, parallel tunnels constructed from a hydrogen-bonded arrangement of urea molecules. These "conventional"

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[**] We are grateful to the EPSRC, the University of Birmingham, and CVCP for financial support.

urea inclusion compounds are characterized by a hexagonal host tunnel structure (space group $P6_122$ or $P6_522$), an incommensurate relationship[13] between the periodicities of the host and guest substructures along the tunnel axis, and substantial dynamic disorder (reorientation about the tunnel axis) of the guest molecules at ambient temperature. In a few cases,[19–23] a distorted tunnel structure is formed at ambient temperature, usually when the length of the guest molecule is close to a simple multiple of the periodic repeat distance of the urea tunnel, which allows a commensurate structure to be formed. Different host structures are also known to be formed with some polymeric guests.[24–27] However, in all of these cases, the urea host structure still comprises continuous 1D tunnels constructed from an essentially infinite 3D hydrogen-bonded network of urea molecules.

Given the similarity of the continuous-tunnel-type host structures in all of these urea inclusion compounds, it would clearly be of interest to find a fundamentally different type of urea host structure in an inclusion compound containing alkane-based guest molecules, and recently[28] we reported the first case of this type. In particular, for 1,7-diaminoheptane ($H_2N(CH_2)_7NH_2$) guest molecules, a new type of layered host–guest structure is formed. Within each layer, there are local segments of urea tunnel structure, which are structurally and topologically very similar to the conventional urea tunnel structure, and the thickness of each layer corresponds to the length of a single guest molecule. Adjacent layers are displaced relative to each other (parallel to the plane of the layers) such that the local segments of tunnel in adjacent layers do not form a continuous tunnel. Adjacent layers are held together through hydrogen bonds to methanol molecules (the solvent normally employed for crystal growth of urea inclusion compounds) that are present in the interlayer region, and the methanol molecules form hydrogen bonds both to urea molecules and to the NH_2 end groups of the 1,7-diaminoheptane guest molecules. Notably, there are no hydrogen-bonding interactions between the NH_2 end groups of the 1,7-diaminoheptane guest molecules and urea molecules. Subsequently,[29] we have shown that for other α,ω-diaminoalkane-guest molecules ($H_2N(CH_2)_nNH_2$; $n = 7–10$, 12) similar layered structures are formed, with the thickness of the layer corresponding to the length of a single guest molecule in each case. Again, there are methanol molecules in the interlayer region, and within the layer, the guest molecule is contained within a segment of tunnel that is structurally very similar to that in the conventional urea inclusion compounds.

Given the apparent robustness of this structure type for those urea inclusion compounds in which the guest molecules contain NH_2 end groups and in the presence of methanol, we now explore whether this structure type may be exploited as a design component in the formation of a more diverse range of structures for urea inclusion compounds. Herein, we recall that alkane ($CH_3(CH_2)_nCH_3$) guest molecules form urea inclusion compounds comprising continuous tunnels, whereas the end groups of α,ω-diaminoalkane ($H_2N(CH_2)_nNH_2$) guest molecules promote the formation of the new layered structure type. We therefore speculate that, for 1-aminoalkane ($H_2N(CH_2)_nCH_3$) guest molecules, the NH_2 end group may promote the formation of layers, but that the CH_3 end group will propagate a continuous tunnel. Thus, we predict that a layered structure analogous to that of the α,ω-diaminoalkane/urea/methanol systems should be formed, but in which the guest component within each layer is the "dimer" unit $H_2N(CH_2)_nCH_3 \cdots H_3C(CH_2)_nNH_2$, which thus gives rise to a bilayer structure, in which the thickness of the layer is approximately double that of the corresponding α,ω-diaminoalkane/urea/methanol material.

To assess this design strategy, crystals were grown from a solution containing 1-aminooctane ($H_2N(CH_2)_7CH_3$) and urea in methanol. Powder X-ray diffraction analysis of the crystals obtained indicates a new structure type, with no detectable amounts of conventional urea inclusion compounds present in the sample.

The structure of the new material was determined from single-crystal X-ray diffraction data,[30] and is found to contain methanol, in addition to urea and 1-aminooctane, with the stoichiometry (1-aminooctane)$_2$(urea)$_{15}$(methanol)$_2$. The structure is monoclinic with space group $C2/c$ and $a = 8.08$, $b = 14.62$, $c = 59.62$ Å, $\beta = 90.61°$. For comparison, the structure of (1,7-diaminoheptane)$_1$(urea)$_7$(methanol)$_2$[28] also has space group $C2/c$, with $a = 8.32$, $b = 13.95$, $c = 29.03$ Å, $\beta = 95.03°$. Clearly the main difference between these structures is the approximate doubling of the c axis in the case of 1-aminooctane. The a and b axes are close to the orthohexagonal description of the ab plane of the host structure in the conventional urea inclusion compounds, and Figure 1 shows the tunnel segments within each layer of the 1-aminooctane/urea/methanol structure. The hydrogen-bonding topology of the urea molecules within these tunnel segments is essentially the same as that in the conventional urea tunnel structure. There are two layers within the repeat unit along the c axis, and the thickness (ca. 29 Å) of each layer is close to the length

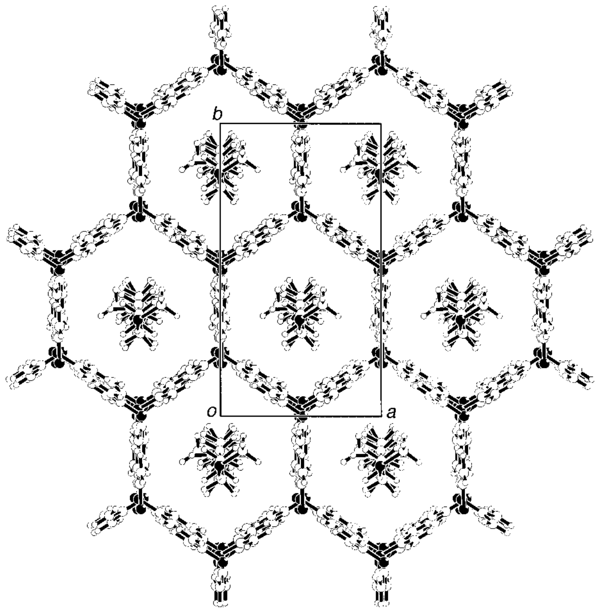

Figure 1. A single host–guest bilayer in the structure of the 1-aminooctane/urea/methanol inclusion compound, viewed along the c axis (perpendicular to the layer). The adjacent bilayer is stacked on top of this bilayer with an offset in the ab plane such that continuous tunnels along the c axis are not formed.

of two 1-aminooctane guest molecules. Within a given layer, all the helical tunnel segments have the same chirality, and the helical tunnel segments in adjacent layers have opposite chirality. The methanol molecules are located between adjacent layers (see Figure 2) and are engaged in hydrogen-bonding interactions with the NH_2 end groups of the 1-aminooctane guest molecules, and with urea molecules at the surface of the layers, in a direct analogy to the structure of the 1,7-diaminoheptane/urea/methanol inclusion compound; this analogy supports the view that this hydrogen-bonding motif is structurally robust, which clearly directs the structure formed in the present case. This view is further supported by the $CH_3 \cdots H_3C$ distance within the guest "dimer" in each layer. In this structure, the $C \cdots C$ distance is 4.761(8) Å, which is significantly longer than the van der Waals contact of two methyl groups (which corresponds to a $C \cdots C$ distance of approximately 4.0 Å, based on twice the van der Waals radius of the methyl group quoted by Pauling[33]). In contrast, a universal feature of conventional urea inclusion compounds is the close packing of the guest molecules along the tunnel,[6, 14] which is an important factor in promoting the incommensurate nature of these materials. For 1-aminooctane/urea/methanol, on the other hand, the main structure-directing effect is the formation of the hydrogen-bonding arrangement (which involves NH_2 end groups, urea molecules, and methanol molecules) at the surface of each layer and within the interlayer region. In the present case, this hydrogen-bonding arrangement is clearly favored at the expense of the optimal guest–guest interaction (corresponding to the van der Waals separation) between adjacent guest molecules within the layer. The formation of the region of locally empty urea tunnel, which arises from the van der Waals "gap" between the CH_3 end groups of adjacent guest molecules in this structure, is a novel feature that is not observed in conventional urea inclusion compounds. One consequence of this structural feature is that the number of urea molecules (15) associated with the $H_2N(CH_2)_7CH_3 \cdots H_3C(CH_2)_7NH_2$ "dimer" unit in the bilayer structure is greater than the number of urea molecules (14) associated with two 1,7-diaminoheptane guest molecules (i.e. in two layers) of the 1,7-diaminoheptane/urea/methanol system. Another consequence is that the density of the 1-aminooctane/urea/methanol crystal (calculated, 1.15 $g\,cm^{-3}$) is appreciably lower than that of the 1,7-diaminoheptane/urea/methanol crystal (calculated, 1.22 $g\,cm^{-3}$).

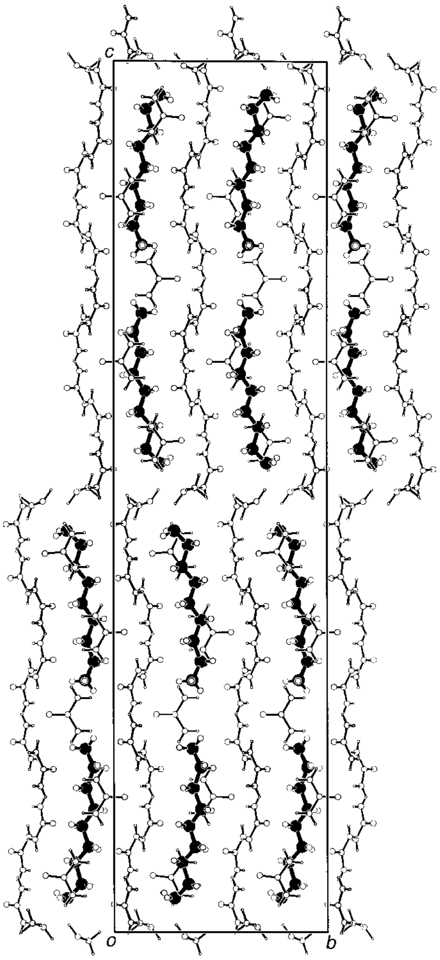

Figure 2. The complete structure of the 1-aminooctane/urea/methanol inclusion compound viewed along the *a* axis. The significant "gap" between the CH_3 end groups of adjacent guest molecules within the bilayer is evident.

The work reported herein demonstrates that the hydrogen-bonding motif formed between NH_2 end groups of aminoalkanes, urea molecules, and methanol molecules is a robust and reproducible structural motif which may be exploited in a structure-directing manner, as illustrated by the formation of the bilayer structure described here.[34] The end group separation (in this case $CH_3 \cdots H_3C$) between adjacent guest molecules within the layer is significantly greater than the van der Waals separation and may be exploited as a means of characterization of such interactions. Indeed, by forming analogous structures for a systematic series of 1-aminoalkanes $H_2N(CH_2)_nCH_3$ as a function of *n*, we may expect to observe a set of different, but in each case well-defined, end-group separation distances.

Received: January 4, 2002 [Z18479]

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[30] Crystal data: $2(C_8H_{19}N)\cdot 15(CH_4N_2O)\cdot 2(CH_4O)$; $M_r = 1223.50$; monoclinic; $a = 8.079(5)$, $b = 14.620(10)$, $c = 59.62(3)$ Å, $\beta = 90.612(9)$; $V = 7041(7)$ Å^3; $T = 273$ K; space group $C2/c$ (no. 15); $Z = 4$; $\mu(\mathrm{Mo_{K\alpha}}) = 0.092$ mm^{-1}. Single-crystal X-ray diffraction data were recorded on a Rigaku R-Axis IIc diffractometer equipped with a molybdenum rotating-anode source and an image-plate detector system. The structure was solved using SHELXS-86[31] and refined using SHELXL-97.[32] The hydrogen atoms of 1-aminooctane were found in the difference Fourier map and their geometry was thereafter restrained. The other hydrogen atoms were placed in calculated positions and a riding model was used for refinement of these atoms. The highest peak (0.45 e Å^{-3}) in the final difference Fourier map was located close (0.6 Å) to one of the CH_2 carbon atoms of the 1-aminooctane guest molecule (the CH_2 group bonded to the CH_3 group)—there was no evidence for "missing" electron density within the "gap" between the CH_3 end groups of adjacent guest molecules within the bilayer. Final R indices: $R1 = 0.084$, $wR2 = 0.24$. CCDC-176977 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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