that this synthesis concept is potentially expandable toward other metal systems. Mixed-metal clusters containing both lanthanides and d block transition elements such as copper, iron, and manganese, for example, may be prepared.[14] The synthetic opportunities abound when the rich varieties of amino acids and transition metals including lanthanide elements are considered. Furthermore, these pentadecanuclear clusters possess unprecedented layered structures that are complex yet architecturally pleasing. The highly ordered arrangement of the metal centers in these nano-sized clusters is expected to yield useful magnetic properties.[5, 7, 8] We believe that the novel structural patterns (and any accompanying physical/chemical properties), coupled with the ability to construct a huge variety of lanthanide clusters will undoubtedly enhance our understanding of lanthanide-based molecular magnetic materials.

Experimental Section

Tyrosine (0.181 g, 1.0 mmol) was added as a solid to an aqueous solution of $Eu(ClO_4)_3$ prepared by dissolution of Eu_2O_3 (1.408 g, 4.0 mmol) in 70% perchloric acid. To this clear solution was added one drop of 1.0 M aqueous HCl and the mixture was stirred at 80 °C for 5 min. The pH value of the above solution was then carefully adjusted by slow addition of 0.5 M aqueous NaOH until the precipitate thus formed remained. The mixture was then filtered and the filtrate was allowed to stand at room temperature. Parallelepipeds of the lanthanide complexes appeared in about one week. The complex was synthesized in a typical yield of 60% (based on tyrosine). Elemental analysis calcd: Eu 37.41; found: 37.36; ESI-MS: *m/z* (%): 1936.1 (30) $[(M^{+}+H) - 5\,H_2O - 2\,ClO_4^{-}]^{3+}$, 1474.7 (100) $[(M^{+}+2\,H) - 2\,ClO_4^{-}]^{4+}$, 1150.9 (40) $[(M^{+}+3\,H) - 8\,H_2O - 2\,ClO_4^{-}]^{5+}$.

Received: January 4, 1999 [Z12870IE]
German version: *Angew. Chem.* **1999**, *111*, 1929–1932

Keywords: amino acids · cluster compounds · coordination modes · lanthanides · template synthesis

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[11] Crystal structure determination of **1**: A colorless crystal (ca. 0.15 × 0.15 × 0.10 mm) was analyzed with a Bruker SMART CCD-based diffractometer at 213 K with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Monoclinic, space group C_2, $a = 32.259(3)$, $b = 20.926(2)$, $c = 22.037(2)$ Å, $\beta = 130.956(4)^{\circ}$, $V = 11234(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.801$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 4.254$ mm^{-1}, $F(000) = 5956$. ω–2θ scans, 29805 reflections measured ($2\theta_{max} = 50^{\circ}$), of which 13780 were independent and all are observed $[I = 2\sigma(I)]$, 528 refined parameters, $R = 0.0812$, $wR_2 = 0.2096$, residual electron density max./min. 2.229/–1.294 e Å^{-3}, max./min. transmission 0.9583/0.7456. Data reduction was performed with the SAINT software, which corrects for Lorentz and polarization factors as well as decay. Absorption corrections were applied with SADABS supplied by G. Sheldrick. The structure was solved by the direct method with the SHELXS-97 program and refined by least squares method on F^2, SHELXL-97, incorporated in SHELXTL-PC version 5.10. Only the metal atoms were refined anisotropically. Hydrogens were calculated by geometrical methods for the ligand and refined as a riding model. The solvated water molecules were found by using the program XWAT, supplied within SHELXTL. No hydrogen atoms were modeled for the hydroxides or water molecules in the cluster or solvated. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-410601.

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A Versatile Route to Porous Solids: Organic–Inorganic Hybrid Materials Assembled through Hydrogen Bonds**

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Destin S. Leinen

One of the many promising applications of supramolecular chemistry is in the design of crystalline host–guest materials, which have been pursued through two principal routes. First, coordination polymers[1] have been shown to form porous materials whose host frameworks can withstand the removal/addition of guest molecules[2] or exhibit high shape specificity in clathration.[3] Second, organic networks have been assembled through directional intermolecular forces[4] to form porous frameworks, which can be applied to homogeneous and heterogeneous[5, 6] separations. Remarkably, some three-dimensional (3D) organic frameworks assembled through hydrogen bonds are rugged enough for reversible guest

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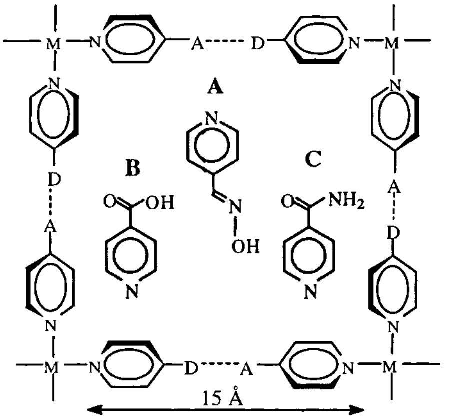
[**] We acknowledge financial support from Kansas State University, NSF-EPSCoR (OSR-9550487), and DuPont, and we thank Dr. R. Rogers and L. Rogers at the University of Alabama, Tuscaloosa (USA) for the X-ray diffraction data for **4**.

inclusion.[6] While it is unlikely that molecular host–guest complexes will be as robust as naturally occurring zeolites, these systems have the advantage of "tunability" where the nature and size of the pore may be altered.[7] We are interested in a crystal engineering strategy based on a combination of the above approaches:[8] while we are inclined to use hydrogen bonds as crystal engineering tools[9] (they can *flex* to accommodate entering and departing guest molecules), we also recognize the advantage of using metal centers (square-planar or octahedral geometries are not easily accessible in organic chemistry). The aim is to assemble metal complexes through hydrogen bonds to form porous materials for inclusion/separation.

The assembly of the materials described herein relies on the ability of Pt^{II} and Ni^{II} ions to coordinate to four pyridine-based ligands in a square-planar arrangement. The ligands are substituted with oxime (**A**), carboxylic acid (**B**), and carboxamide (**C**) moieties (Scheme 1); such functional groups can overcome competition from solvent molecules and counterions to assemble linear silver(I) complexes through complementary hydrogen bonds.[10] Successful assembly of square-planar complexes through head-to-head hydrogen-bond interactions between the ligands affords the potential for large cavities, 15 Å × 15 Å, that are suitable for inclusion of guest molecules (Scheme 1; cavity sizes are consistently estimated allowing for van der Waals radii). As ever, the possibility for interpenetration exists,[11] but even in that case, such large voids should only be partially filled (although examples to the contrary have been reported[12]). Herein, we describe four structures which demonstrate the proclivity of platinum(II) and nickel(II) complexes to form crystalline host–guest materials.



Scheme 1. A = Hydrogen-bond acceptor, D = hydrogen-bond donor, M = metal ion.

In compound **1**,[13] the metal complexes link through four unique N–H⋯O amide–amide hydrogen bonds to form cationic sheets (Figure 1); the hydrogen-bond motif results in the formation of two unique holes in each parallel sheet. The smaller, $R_4^4(16)$ hole[14] is blocked by nickel(II) ions in the sheets above and below, but the larger, $R_2^2(28)$ holes only partially overlap, forming channels for the perchlorate counterions.[15] Additional hydrogen bonds between coordinated water molecules and amide oxygen atoms connect the sheets above and below to generate the three-dimensional network. As the amide–amide hydrogen bonds display catemer-type interactions (instead of head-to-head), the large holes predicted for these assemblies are not realized, and instead small channels containing counterions are present.

$[Ni(\mathbf{C})_4(H_2O)_2][ClO_4]_2 \cdot 2\,H_2O$ **1**

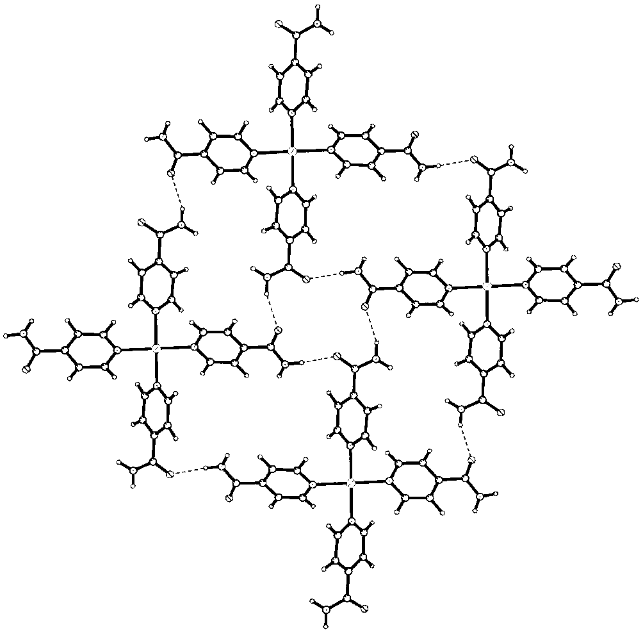


Figure 1. An infinite cationic layer in **1**, in which two unique holes $R_4^4(16)$ and $R_2^2(28)$ are formed.

The versatility of the strategy is demonstrated in compound **2**, which utilizes a different type of hydrogen-bonding moiety (oxime instead of amide). The oxime hydroxy groups link through complementary O–H⋯O hydrogen bonds to form sheets with large, $R_4^4(64)$ hourglass-shaped holes (22 Å long, 15 Å wide at the ends, 7 Å wide at the waist). The sheets are cross-linked by hydrogen bonds between the axially coordinated water molecules and the bromide counterions, forming a 3D network, where the large holes are aligned into channels. Twofold interpenetration of the 3D networks blocks the center of the large hole, leaving two smaller channels at each end. In this case, a host–guest complex is formed, and the guest molecules, 4-aldoximepyridine, are contained inside the channels (Figure 2), held in the lattice by hydrogen bonds to the bromide ion and the ligated oxime moieties.[16] Thus, the structure of **2** demonstrates that an octahedral system can generate a 3D network with holes large enough to hold small organic molecules.

$[Ni(\mathbf{A})_4(H_2O)_2]Br_2 \cdot 2\,\mathbf{A}$ **2**

A similar square-planar system can also create a host–guest complex, as evidenced by compound **3**. In this case, *trans* ligands are linked linearly by head-to-head $[R_2^2(8)]$ amide–amide hydrogen bonds; the resulting chains are arranged parallel to each other. The linear assemblies are

$[Pt(\mathbf{C})_4]Cl_2 \cdot 4\,\mathbf{C}$ **3**

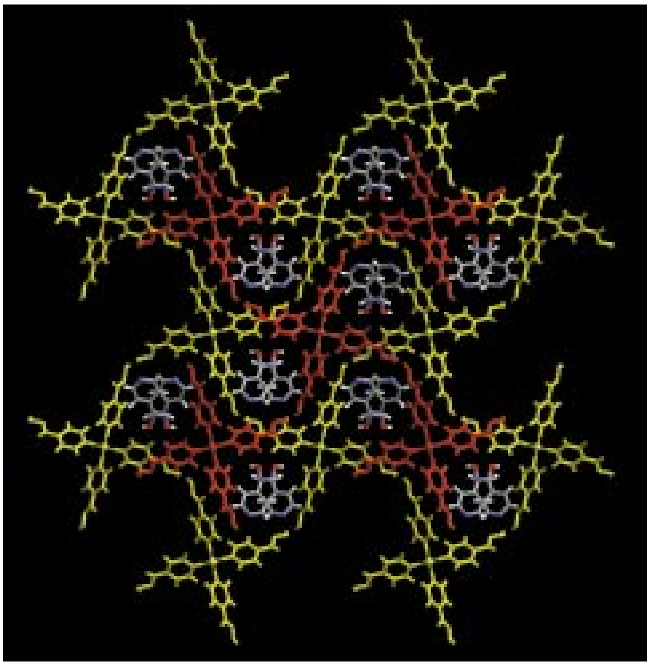


Figure 2. The structure of **2** looking down channels containing guest 4-aldoximepyridine molecules, where interpenetrating hydrogen-bonded nets are depicted in yellow and red, respectively.

interconnected perpendicular to the propagation of the chains through two inequivalent N–H ··· Cl interactions, creating a three-dimensional network which contains large square channels (Figure 3 left). The guest isonicotinamide molecules occupy these channels (Figure 3 right), and are anchored to the lattice by hydrogen bonds. Compound **3** demonstrates that even if the structure manifests head-to-head hydrogen bonds in chains (1D), rather than the sheets (2D) proposed in Scheme 1, other hydrogen-bonding interactions can create a 3D framework, and the smaller channels are still large enough to hold small organic molecules.

While the amide and oxime ligands remain protonated, thus necessitating the presence of counteranions, carboxylic acid moieties can become deprotonated, and the lattices can be constructed without counterions. Thus compound **4**, unlike

$Pt(H\mathbf{B})_2(\mathbf{B})_2 \cdot 2H_2O$ **4**

1–**3**, is a neutral metal complex which forms two crystallographically unique square nets, assembled through charge-assisted carboxylate–carboxylic acid hydrogen bonds [$R_4^4(56)$] (Figure 4). The distance between the platinum(II) ions in each sheet is >15 Å, leading to large square cavities. The crystal structure of **4** provides a rare example of inclined interpenetration of (4,4) nets in three mutually perpendicular planes.[11] Each square cavity of one of the unique nets is

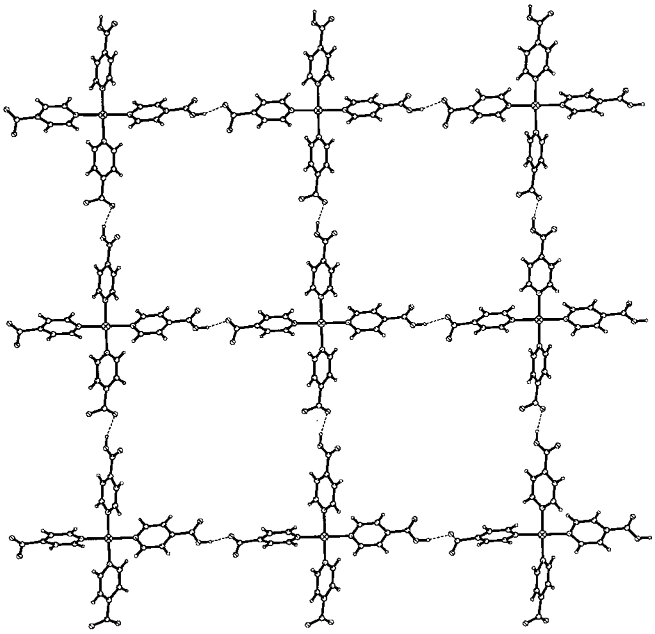


Figure 4. One of the 2D hydrogen-bonded nets in **4**, showing the large square cavities generated by hydrogen-bonded metal–complex cations.

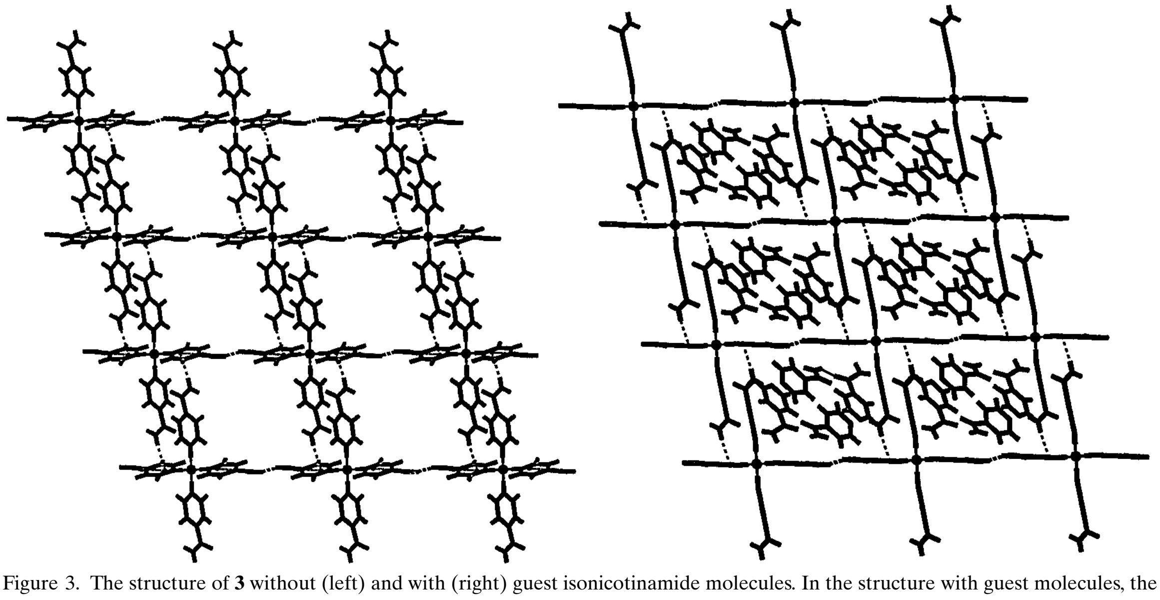


Figure 3. The structure of **3** without (left) and with (right) guest isonicotinamide molecules. In the structure with guest molecules, the ligand pyridine rings are replaced with a line for clarity.

interwoven by three other nets, while those of the other unique net are interwoven by five nets. Despite this interpenetration, channels are present which host disordered water molecules (Figure 5). The complex is thermally stable, with a melting point of $>300\,^{\circ}$C, indicating that the structure could remain intact for reversible addition of water or other guests in the channels.

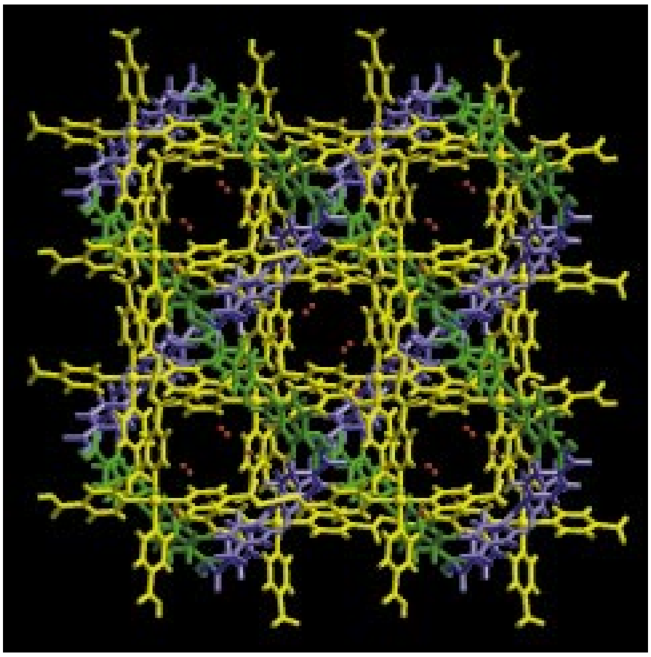


Figure 5. The structure of **4**, viewed down channels resulting from interpenetrating hydrogen bonded nets. The three mutually perpendicular nets are shown in purple, yellow, and green. The red spheres are guest water molecules.

Experimental Section

1: An aqueous solution (20 mL) of isonicotinamide (0.30 g, 2.5 mmol) was slowly added to an aqueous solution (10 mL) of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.18 g, 0.49 mmol). The solution was allowed to evaporate at room temperature. Irregular blue crystals formed in a few weeks (m.p. $>300\,^{\circ}$C).

2: A solution of 4-aldoximepyridine (0.20 g, 1.64 mmol) in ethanol was slowly added to an aqueous solution of $NiBr_2 \cdot xH_2O$ (0.14 g). The flask was covered and left to stand in ambient conditions. Slow evaporation of solvent produced blue, platelike crystals (m.p. $>300\,^{\circ}$C).

3: An aqueous solution of isonicotinamide (0.08 g, 0.66 mmol) was added to an aqueous solution of $[NH_4]_2[PtCl_4]$ (0.05 g, 0.13 mmol), and allowed to evaporate at room temperature. After about one week, a yellow powder was filtered off and washed with ethanol. The ethanolic filtrate and the mother liquor were mixed and allowed to evaporate, yielding irregular colorless crystals (m.p. $>300\,^{\circ}$C).

4: A 1:2 ethanol:water solution (30 mL) of isonicotinic acid (0.13 g, 0.94 mmol) was added to an aqueous solution (15 mL) of $K_2[PtCl_4]$ (0.07 g, 0.17 mmol) and allowed to evaporate, yielding conical colorless crystals (m.p. $>300\,^{\circ}$C). Typically, the yields were over 80% except in the case of **4**, which was below 40%.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-108604–CCDC-108607 (**1**–**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: November 16, 1998 [Z12665IE]
German version: *Angew. Chem.* **1999**, *111*, 1932–1936

Keywords: crystal engineering · host–guest chemistry · hydrogen bonds · nickel · platinum

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[13] X-ray diffraction studies were performed on single crystals using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 173 K, and Lorentz and polarization corrections, and semiempirical absorption corrections were applied for all compounds. Structure solutions were determined from Patterson methods using SHELXS-86 with a full-matrix least-squares refinement on F^2 using SHELXL-93 (G. Sheldrick, Universität Göttingen). Hydrogen atoms were located from the difference map, and a riding model with fixed thermal parameters [$u_{ij} = 1.2U_{ij}$(eq) for the atom to which they are bonded] was used for subsequent refinements. Crystal data: Compound **1**, $0.4 \times 0.3 \times 0.1$ mm, monoclinic, space group $C2/c$, $a = 18.492(3)$, $b = 10.076(1)$, $c = 18.665(4)$ Å, $\beta = 91.03(1)^{\circ}$, $V = 3477(1)$ Å^3, $\rho = 1.563$ Mg m^{-3}, 3066 unique reflections, 2251 observed ($I > 2\sigma I$), 261 parameters, $R = 0.0491$, $R_w = 0.1085$. Compound **2**, $0.4 \times 0.3 \times 0.3$ mm, orthorhombic, space group $Aba2$, $a = 22.414(2)$, $b = 23.753(2)$, $c = 8.0830(7)$ Å, $V = 4303.6(7)$ Å^3 $\rho = 1.524$ Mg m^{-3}, 2888 unique reflections, 2191 observed ($I > 2\sigma I$), 268 parameters, $R = 0.0494$, $R_w = 0.1171$. Compound **3**, $0.4 \times 0.2 \times 0.2$ mm, monoclinic, space group $P2_1/c$, $a = 13.533(1)$, $b = 9.6166(8)$, $c = 20.787(2)$ Å, $V = 2569.4(4)$ Å^3, $\rho = 1.607$ Mg m^{-3}, 4530 unique reflections, 3444 observed ($I > 2\sigma I$), 340 parameters, $R = 0.0281$, $R_w = 0.0723$. Compound **4**, $0.7 \times 0.2 \times 0.2$ mm, tetragonal, space group $P4_32_12$, $a = 16.2242(4)$, $c = 22.8441(8)$ Å, $V = 6013.1(3)$ Å^3, $\rho = 1.585$ Mg m^{-3}, 7137 unique reflections, 6079 observed ($I > 2\sigma I$), 356 parameters, $R = 0.0584$, $R_w = 0.1436$, a disordered carboxylate unit was restrained with fixed distances (rC–C 1.54; rC–O 1.26).

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Photoionization and Electron Transfer of Biphenyl within the Channels of Al-ZSM-5 Zeolites

Isabelle Gener, Guy Buntinx, and Claude Brémard*

There is considerable interest in the use of crystalline aluminosilicate porous materials such as zeolites to study and try to control the photophysical and photochemical properties of the occluded molecules.[1] The ability of zeolites to stabilize radical cations and trap electrons is now firmly established.[2, 3] In contrast, the reverse situation in which zeolites act as electron donors is far less documented.[4, 5] The ZSM-5 zeolites with straight (0.54 × 0.56 nm) and zigzag (0.51 × 0.55 nm) channels have been reported previously to generate radical cations spontaneously and stabilize them in the void space.[6] While the mechanism of oxidation remains unclear today, it appears that the presence of aluminum in the zeolite is a requirement for persistent radical cations. Herein we present our most striking results concerning the photolysis of biphenyl ($C_{12}H_{10}$, BP) occluded at low coverage in nonacidic ZSM-5 zeolites. The emphasis of the paper is mainly set on the photoionization of biphenyl and electron transfer. The zeolite – radical cation – electron interactions have been tuned by varying the silicon:aluminum ratio, by using charge-balancing cations, and without any additional molecules.

Weighted amounts of bisublimated BP (0.5 – 1 BP per unit cell) were mixed with freshly dehydrated $M_n[Al_nSi_{96-n}O_{192}]$ ($M = Na^+$, K^+, Cs^+; $n = 0$, 3, 6) zeolites under an inert atmosphere in a silica cell. The FT-Raman and diffuse reflectance UV/Vis absorption spectra of the mechanical powder mixtures were recorded as a function of time. All the spectroscopic data recorded after the required equilibration period of one month at a gentle temperature (50 °C) are typical of occluded BP at low coverage within the void space. The aluminum content, the extraframework cations M^+, and the cosorbed gas (argon or helium) do not induce dramatic effects upon the molecular conformation of ground state BP (BP(S_0)) as evident from similar vibrational spectroscopic characteristics to that reported previously for BP(S_0) in fluid solution and attributed to a twisted structure.[7] The ground-state absorption electronic spectra of BP occluded at low coverage in ZSM-5 are typical of isolated chromophores.[7]

Molecular mechanics calculations (MM), Monte Carlo simulations (MC), and molecular dynamics calculations (MD) provide evidence of the expected location, the structure as well as the diffusion of BP(S_0) within the void space of the $Na_4[Al_4Si_{92}O_{192}]$ zeolites.[8] The BP(S_0) molecules were found to be located preferentially in the straight channels in the vicinity of the intersection with zigzag channels (Figure 1). The expected site of BP(S_0) in ZSM-5 is in reasonable agreement with preliminary X-ray diffraction data performed at high coverage.[9]

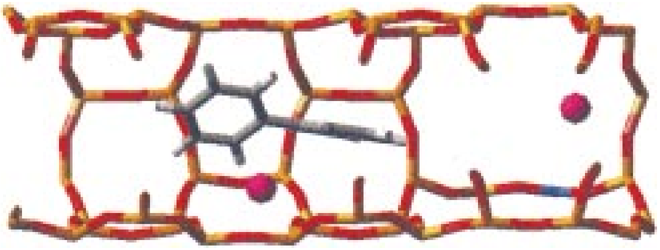
Figure 1. Cross-sectional view of biphenyl (BP, S_0) occluded in the straight channel of $Na_4Si_{92}Al_4O_{192}$ zeolite perpendicular to the b axis. The yellow Si, blue Al, and red O cylinders represent the ZSM-5 framework, the pink balls represent the extra-framework Na^+ cations, the shaded and white cylinders represent the C and H atoms of BP, respectively.

It should be noted that the nearest C ⋯ Na and C ⋯ Al distances are found to be 4.66 and 7.1 Å, respectively. From MD simulations data the main role of the zeolite framework appears to be to reduce the mobility of BP within the void space, and the BP(S_0) molecule performs only vibrational, internal rotation, and translational motions in the vicinity of the sorption site.[8]

An excimer laser (248 nm, 15 ns, 0.12 – 30 mJ cm^{-2}) was used as pump excitation within the $S_3 \leftarrow S_0$ ($\pi^* \leftarrow \pi$) transition of occluded BP in $M_n[Al_nSi_{96-n}O_{192}]$. This transition exhibits an intense electronic absorption around 250 nm. Decays in the UV/Vis spectra up to 300 μs were recorded after the laser photolysis of the $1BP/Si_{96}O_{192}$ and $1BP/Na_3[Al_3Si_{93}O_{192}]$ samples by the transient diffuse reflection technique.[10] It should be noted that with the pump excitation power used, no transient spectra were obtained after photolysis of the bare zeolites.

The data processing[11] of the transient spectra provides clear evidence of the pure component spectra and concentrations of the lowest triplet state BP(T_1) (355 nm) and the radical cation $BP^{+\bullet}$ (380, 660 nm) within the experimental pump energy range.[7] No spectral evidence of both the radical anion and trapped electron was found in either $1BP/Si_{96}O_{192}$ or $1BP/Na_3[Al_3Si_{93}O_{192}]$ samples under the experimental conditions used.[7, 8, 12, 13] The short lifetime of BP(T_1) is found to be shorter in $1BP/[Si_{96}O_{192}]$ (3×10^{-7} s) than in $1BP/Na_3[Al_3Si_{93}O_{192}]$ (2.4×10^{-6} s). In contrast, the lifetime of $BP^{+\bullet}$

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