

An Ordered Form of the Extra-Large-Pore Zeolite UTD-1: Synthesis and Structure Analysis from Powder Diffraction Data

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Received March 9, 1999

Abstract: A highly crystalline sample of the extra-large-pore, high-silica zeolite UTD-1 has been prepared in fluoride medium. The resulting product (UTD-1F) has a powder diffraction pattern remarkably different from that published for the calcined form of conventionally prepared UTD-1, and it could only be indexed on a monoclinic unit cell. The crystal structure was determined ab initio in the space group $P2_1/c$ from synchrotron powder diffraction data collected on a textured sample. The resulting structure, with 69 non-H atoms in the asymmetric unit, is by far the largest structure solved directly from powder diffraction data to date. Subsequent Rietveld refinement of the structure in Pc , with 349 positional parameters and 464 geometric restraints, proved to be surprisingly stable and converged with $R_F = 0.041$ and $R_{wp} = 0.134$ ($R_{exp} = 0.101$). In contrast to the structure reported for calcined UTD-1, no evidence of disorder was found in the UTD-1F framework (structure type code **DON**). There is a strict up–down alternation of the orientation of the Si tetrahedra in the 14-rings, and double crankshaft chains link adjacent 14-ring channels. Not only the framework, but also the $(Cp^*)_2Co$ complex, which appeared very clearly on the difference electron density map, was found to be fully ordered in the channels with the 5-fold axis parallel to the channel direction.

Introduction

With the synthesis of UTD-1 in 1995, a new approach to zeolite synthesis was unveiled. By using the organometallic complex bis(pentamethylcyclopentadienyl)cobalt(III) hydroxide ($[(Cp^*)_2Co]OH$) as the structure directing agent, Balkus and co-workers¹ were able to produce a novel high-silica zeolite with 14-ring pore openings.² It was the first extra-large-pore silicate-based zeolite ever synthesized. Earlier studies with the smaller cobalticinium ($[(Cp)_2Co]^+$) ion as a structure-directing agent had produced clathrasil phases with the **NON**, **AST**, and **DOH** topologies,^{3,4} but no silicate-based materials with an accessible pore system (though more recently, UTD-12, which does have accessible channels, has been prepared with use of the cobalticinium ion⁵). Structural characterization of the calcined form of UTD-1 indicated that it was disordered along the one-dimensional 14-ring channel, but this did not affect the size of the pores, just the topology of the channel walls.⁶

In the hope of improving the quality of the crystalline product, a synthesis of UTD-1 in fluoride medium was attempted. It is

known that the use of fluoride as a mineralizer in hydrothermal syntheses of silica-based zeolites promotes the formation of larger crystals of high quality.⁷ Scanning electron micrographs of the resulting sample, hereafter referred to as UTD-1F, showed it to consist of bundles of well-formed, but very fine, needlelike crystallites with dimensions of ca. $0.5 \times 0.5 \times 40 \mu m^3$ (Figure 1). The morphology was similar to that described by Lobo et al. for calcined UTD-1,⁶ but the X-ray powder diffraction pattern seemed to be quite different. Furthermore, the peaks in the pattern were all very sharp, giving no obvious indication of disorder in the structure. It appeared that the structure of UTD-1F was likely to be ordered and significantly different from that reported for calcined UTD-1. Its structure would have to be determined before structure refinement could be envisaged.

Fortunately, the UTD-1F sample seemed to be particularly well-suited for the application of a new approach to structure solution from powder diffraction data that we had been developing.⁸ The method exploits the fact that additional information can be extracted from an oriented polycrystalline sample, but of course has the prerequisite that an oriented sample be available. Needlelike crystallites, such as those of UTD-1F, lend themselves to orientation, and a suitably textured sample of UTD-1F could, in fact, be prepared. The necessary diffraction data were then collected, and a full structural investigation was undertaken.

Experimental Section

Synthesis. A silica slurry, prepared from 27.8 g of Cabosil M5 (Aldrich) and 68.4 g of water, was stirred until homogeneous. A 6.60 g sample of this slurry was added to 49.15 g of an 8.95 wt % aqueous

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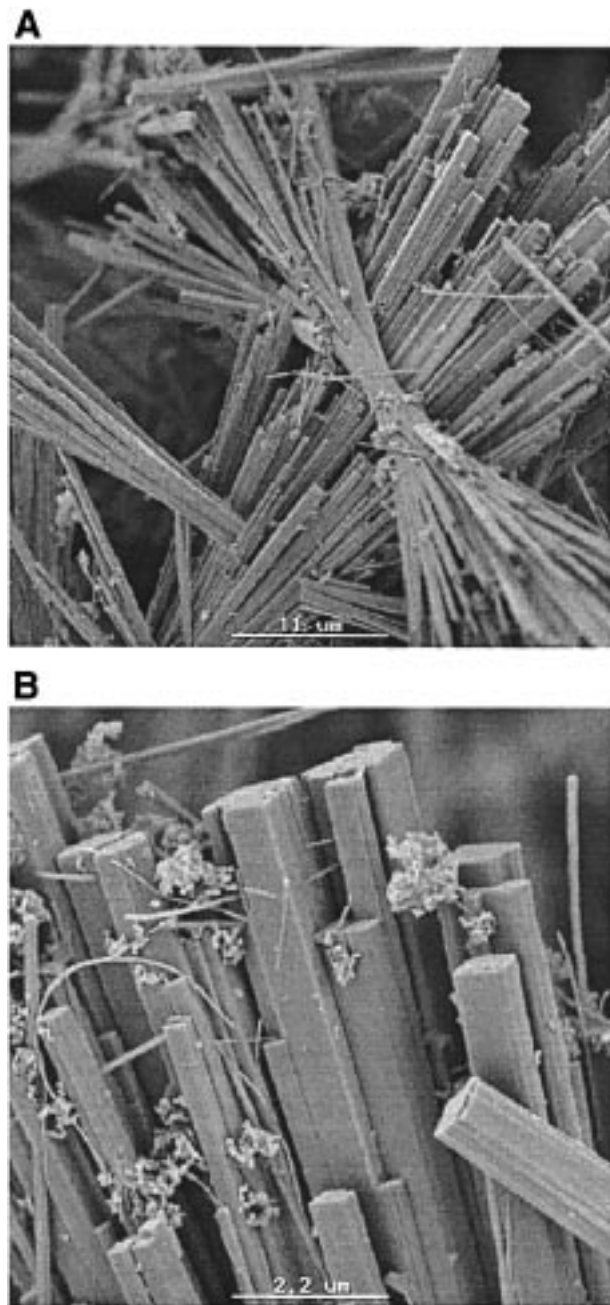


Figure 1. Scanning electron micrograph of UTD-1F (A) showing a typical bundle of fine needles and (B) a close-up of the ends of the needles.

$[(\text{Cp}^*)_2\text{Co}]\text{OH}$ solution and the mixture was stirred with a magnetic stirrer for 1.5 h. A solution of 0.67 g of aqueous 38 wt % HF (J. T. Baker) in about 70 g of water was slowly added to the synthesis mixture. After 20 min of vigorous stirring, the homogeneous gel was concentrated by removing excess water under reduced pressure. The remaining 24.2 g of the uniform gel was transferred to a Teflon-lined autoclave (Berghoff, 35 mL) and heated to 170 °C for 25 days. The molar composition of the gel was 100 SiO_2 :40 $[(\text{Cp}^*)_2\text{Co}]\text{F}$:3125 H_2O . Finally, the zeolite was isolated by filtration and washed extensively with water. The yield of as-synthesized UTD-1F was 2.05 g.

Scanning Electron Microscopy. High-resolution scanning electron microscopy (SEM) photographs were taken with a JEOL JSM-6000F on a platinum-coated sample.

Chemical Analysis. Chemical analysis was performed by Service Central d'Analyse du CNRS, Vernaison, France. The Si and Co content was determined by inductively coupled plasma emission spectroscopy, C by coulometry after calcination of the sample under oxygen, and F by using a fluoride ion selective electrode after mineralization.

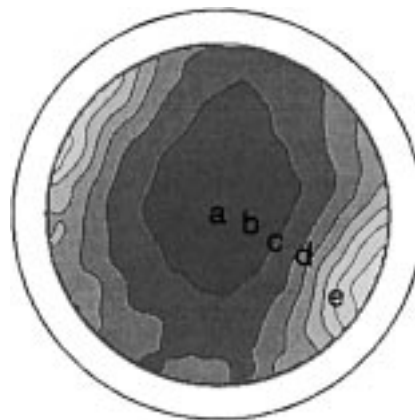


Figure 2. Pole figure for the 011 reflection. Tilt angle χ increases along the radius (0° at the center and 90° at the outermost circle), and the rotation angle ϕ increases counterclockwise around the perimeter of the circle (0° at the right). Intensity is proportional to the degree of grayness. Sample tilt and rotation angles selected for the collection of full diffraction patterns (see Figure 3) are indicated.

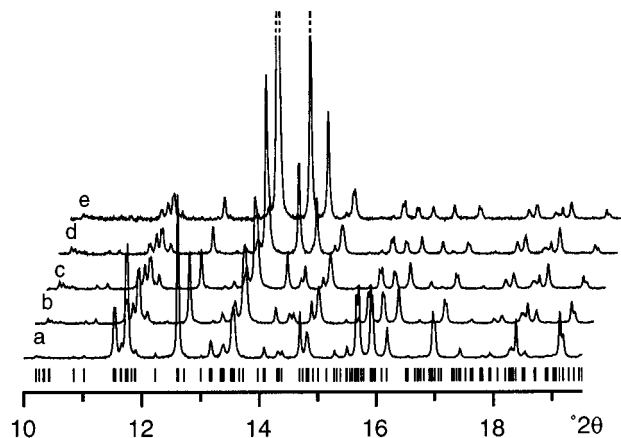


Figure 3. Small sections of the five diffraction patterns collected at different sample tilt (χ) and rotation (ϕ) angles. (a) $\chi = 0^\circ$, $\phi = 0^\circ$; (b) $\chi = 20^\circ$, $\phi = 345^\circ$; (c) $\chi = 35^\circ$, $\phi = 335^\circ$; (d) $\chi = 50^\circ$, $\phi = 335^\circ$; and (e) $\chi = 70^\circ$, $\phi = 325^\circ$.

MAS NMR Spectroscopy. The ^{19}F and ^{29}Si MAS NMR spectra were recorded on a Bruker DSX 400 spectrometer.

Powder Diffraction Data Collection for Structure Determination. The needlelike crystallites were aligned by using shear forces in a polystyrene matrix, and the hardened sample was then polished and inserted into a circular flat-plate sample holder.

A texture goniometer was attached to the powder diffractometer on the Swiss-Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble to allow the sample to be rotated and tilted in a controlled manner during the data collection. A pre-detector analyzer crystal, which acts as a very fine receiving slit and allows full advantage to be taken of the parallel beam geometry, was also mounted. The parallel nature of the synchrotron beam is an essential feature of the experiment, because it makes the collection of high-resolution data at all sample tilt angles possible.

To determine the orientation of the crystallites in the sample, pole-figure data (variation of the intensity of a single reflection as a function of sample tilt (χ) and rotation (ϕ)) were measured for seven single (nonoverlapping) reflections. As an example, the pole figure for the 011 reflection is shown in Figure 2. Full diffraction patterns were then collected at five different sample orientations, selected on the basis of the pole-figure data to give maximum contrast. The differences in the relative intensities measured at different sample tilt and rotation angles are readily apparent in the small sections of the five diffraction patterns shown in Figure 3.

Powder Diffraction Data Collection for Structure Refinement. High-resolution synchrotron powder diffraction data were also collected

Table 1. Powder Diffraction Data Collection Details for UTD-1F

Texture Measurement	
synchrotron facility	SNBL at ESRF
sample	textured, flat plate
wavelength (Å)	0.99747(1)
analyzer crystal	Si 111
pole-figure data	
reflens (<i>hkl</i> , deg 2θ)	10 $\bar{2}$, 4.887; 011, 7.026 111, 8.252; 013, 8.939 11 $\bar{3}$, 9.230; 316, 16.182 326, 22.889
step size in χ (deg)	5
step size in ϕ (deg)	5
time per step (s)	2–4
time/background step (s)	15
full diffraction patterns	
sample orientations	$\chi = 0^\circ, \phi = 0^\circ; \chi = 20^\circ, \phi = 345^\circ$ $\chi = 35^\circ, \phi = 335^\circ; \chi = 50^\circ, \phi = 335^\circ$ $\chi = 70^\circ, \phi = 325^\circ$
2θ range (deg 2θ)	3.0–58.5
step size (deg 2θ)	0.01
time per step (s)	3–17
Capillary Measurement	
synchrotron facility	SNBL at ESRF
sample	1 mm capillary
wavelength (Å)	0.64796(1)
analyzer crystal	Si 111
2θ range (deg)	1.8–37.0
step size (deg 2θ)	0.007
time per step (s)	4–15

on an untextured capillary sample of UTD-1F with a Debye–Scherrer diffractometer geometry and an analyzer crystal. To improve the counting statistics at higher 2θ angles, the pattern was divided into three 2θ regions, and the time per step for each region set accordingly. The data were normalized by using the monitor counts.

Further details of both data collections are given in Table 1.

Results

Chemical Composition. Elemental analysis yielded the following composition (in wt %): 39.705 Si, 2.675 Co, 10.15 C, 0.63 F (molar ratios 32 Si:1.03 Co:19.13 C:0.75 F). The slight deficiency in C is probably within the error of the analysis, but that for F appears to be real. For charge balance, it is assumed that OH[−] ions are also present in the material. This corresponds to the idealized chemical formula (normalized to 64 Si per unit cell) [Si₆₄O₁₂₈]·2(Cp*)₂CoF_{0.75}OH_{0.25}.

MAS NMR Spectroscopy. The ¹⁹F MAS NMR spectrum for UTD-1F consists of a single signal at −64 ppm. This is comparable to that observed for ZSM-5 prepared in fluoride medium.⁹ The ²⁹Si MAS NMR spectrum contains a broad band of unresolved peaks in the range 104–117 ppm.

Structure Determination. The powder diffraction pattern of UTD-1F was indexed on a monoclinic unit cell with the program TREOR90.¹⁰ The refined values of the lattice parameters from the Rietveld refinement are given in Table 2. Systematic absences were indicative of the space group *P2₁/c*.

As mentioned in the Introduction, the structure was determined by using a newly developed method, which requires that the crystallites in the polycrystalline sample be oriented preferentially rather than randomly. The rationale for this approach is that a sample with pronounced preferred orientation can be regarded as being something between an “ideal” powder (with randomly oriented crystallites) and a single crystal. That

Table 2. Rietveld Refinement Details

crystal chemical formula	[Si ₆₄ O ₁₂₈]·2(Cp*) ₂ -CoF _{0.75} OH _{0.25}
lattice parameters	
space group	<i>Pc</i>
<i>a</i> (Å)	14.9701(1)
<i>b</i> (Å)	8.4761(1)
<i>c</i> (Å)	30.0278(2)
β (deg)	102.65(1)
Rietveld refinement	
standard peak for peak shape function (<i>hkl</i> , deg 2θ)	10 $\bar{2}$, 3.17°
peak range (fwhm)	25
no. of observations (steps, <i>N</i>)	4994
no. of contributing reflens	3519
geometric restraints [no.]	
Si–O, Å	1.61(1) [128]
O–Si–O, deg	109.5(8) [192]
Si–O–Si, deg	145(5) [64]
Co–C(ring), Å ^a	2.040(5) [10]
C(ring)–C(ring), Å ^a	1.420(1) [10]
C(ring)–C(Me), Å ^a	1.520(1) [10]
C(ring)–C(ring)–C(ring), deg ^a	108.0(1) [10]
C(ring)–C(ring)–C(Me), deg ^a	126.0(1) [20]
C(Me)···C(Me) to maintain planarity ^a	[20]
total no. of restraints	464
no. of structural parameters (<i>P1</i>)	355
no. of profile parameters (<i>P2</i>)	11
$R_{\text{exp}} = [(N - P1 - P2)/\sum w y^2(\text{obs})]^{1/2}$	0.101
$R_{\text{wp}} = \{\sum w [y(\text{obs}) - y(\text{calc})]^2 / \sum w y^2(\text{obs})\}^{1/2}$	0.134
$R_{\text{F}} = \sum F(\text{obs}) - F(\text{calc}) / \sum F(\text{obs})$	0.041

^a The weights of the restraints on the (Cp*)₂Co complex were set high to maintain a rigid-body approximation.

is, much more information can be extracted from the diffraction data of such a sample, provided they are measured appropriately. A two-step procedure is used to extract a set of near single-crystal quality reflection intensities from the data. First, the texture of the sample (the distribution of crystallite orientations) is determined from the pole-figure data. Then, by using this information to quantify the relationship between the full diffraction patterns, a single set of reflection intensities is extracted. In this way, information regarding the relative intensities of overlapping reflections can be better estimated. A detailed description of the method is in preparation, but the main points are outlined in ref 8.

The texture of the UTD-1F sample was determined from the seven measured pole figures with the program package BEAR-TEX,¹¹ and then a set of integrated intensities were extracted from the five full diffraction patterns with use of a program we have developed for this purpose. These intensities were used as input to the direct methods programs in the single-crystal program package Xtal3.2.¹² In the top 40 peaks of the initial E-map, 16 Si atoms, which described a complete 3-dimensional, 4-connected framework with 14-ring pores (Figure 4), and even 17 of the bridging oxygens were found. Subsequent difference electron density maps generated by using the *pseudo*-single-crystal data allowed the remaining 15 oxygens and the (non-framework) Co to be located.

The texture method yields a good estimate of the relative intensities of overlapping reflections for the application of direct methods of structure solution, where approximate intensities suffice. However, the procedure involves a number of approximations, so the intensities are not accurate enough for detailed structure refinement. For this reason, further structure

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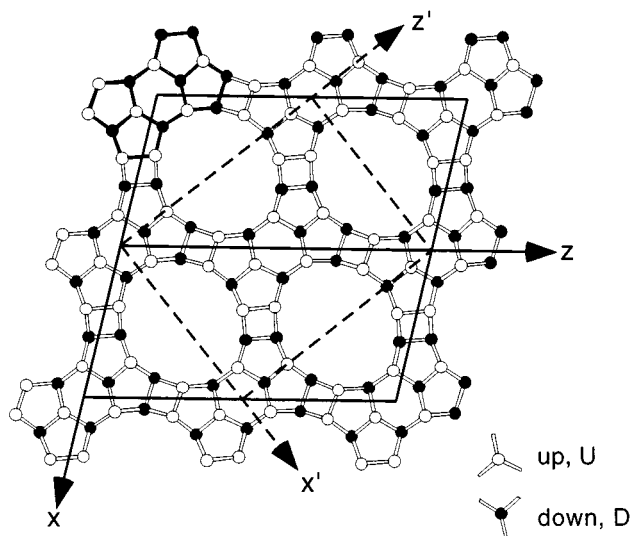


Figure 4. Framework structure of UTD-1F showing the relationship between the topological orthorhombic unit cell (dashed line) and the observed monoclinic one (full line). Filled and open circles indicate Si tetrahedra pointing down into the page and up out of the page, respectively. Bridging oxygen atoms have been omitted for clarity. A “butterfly” unit in the upper left-hand corner is highlighted.

analysis was performed with the diffraction data collected on the untextured sample of UTD-1F.

Rietveld Refinement. Rietveld refinement with the program XRS-82¹³ was initiated by using the structural model described above. First, the framework was refined with only the high-angle diffraction data and strong geometric restraints on the framework atom bond lengths and angles. Then, a difference electron density map, generated by using this model and the whole diffraction pattern, revealed very clearly where the pentamethylcyclopentadienyl (Cp*) rings coordinated to the Co were located in the 14-ring channels. However, the short distances between symmetry-related Co complexes required that the occupancy parameters for these nonframework atoms be restricted to 1/2, and a disordered model for the template assumed.

Strong restraints on the bond lengths and angles of the Co complex were then imposed to keep it chemically sensible, while its orientation was refined in a *pseudo*-rigid-body fashion. However, further refinement did not improve the fit, and the *R* values could not be reduced below $R_F = 0.118$ and $R_{wp} = 0.309$. The refinement of the [(Cp*)₂Co]⁺ ion remained unstable, and significant intensity differences for a number of reflections were observed in the profile plot, so a reduction of the symmetry to *Pc* was attempted. This symmetry reduction dictated that the number of framework atoms in the asymmetric unit be doubled, yielding a model with 32 Si, 64 O, 1 Co, and 20 C atoms in the asymmetric unit. The corresponding increase in the number of positional parameters from 207 to 349 appeared to be rather problematic for a Rietveld refinement, where conventional wisdom suggests that up to 200 parameters can be refined sensibly. However, much to our surprise, the profile fit improved tremendously and the refinement became stable in the lower space group. Furthermore, an ordered model for the Co complex (i.e. full occupancies) could be refined. The arrangement of the Co complex in the channels and the difference electron density map generated in *Pc* by using just the framework and the Co as a model are shown in Figure 5.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for UTD-1F

Si—O		Si—O—Si	
min	1.58(4)	min	131(2)
max	1.64(3)	max	169(2)
av	1.61	av	150
O—Si—O		C(Me)—O	
min	107(2)	min	2.93(7)
max	112(2)	max	3.87(6)
av	109.5	av	3.44

To approximate the contribution from the H atoms of the methyl groups of the Cp* rings, the population parameters of the respective carbon atoms were increased from 1.0 to 1.5 (six electrons for the C and one for each of the three H atoms). With this model, the weight of the geometric restraints with respect to the diffraction data on both the framework and the Co complex (*pseudorigid* body) could be reduced to 1, and the refinement of the atomic positions remained stable and chemically sensible. Five displacement factors were refined: one each for Si, O, Co, C(ring), and C(Me). The displacement factors for the C(Me) atoms refined to relatively large values, but that is consistent with single-crystal structure analyses of other materials containing this complex.¹⁴ Refinement of the occupancy of the (Cp*)₂Co species resulted in a population parameter of 0.98(1), so it was reset to exactly 1.0. Neutral atomic scattering factors were used for all atoms. Final refinement of this model converged with $R_F = 0.041$ and $R_{wp} = 0.134$ ($R_{exp} = 0.101$). The final Rietveld profile fit is shown in Figure 6.

Although both the chemical analysis and the ¹⁹F MAS NMR spectrum indicated that F⁻ ions are present in the structure, they could not be located. The final difference Fourier map showed no significant peaks, so they are probably disordered over several different sites (see Discussion).

Further details of the refinement are given in Table 2. The atomic parameters for the final structure are available as Supporting Information. A few selected interatomic distances and angles are listed in Table 3.

Discussion

The determination of such a complex structure (69 non-H atoms in *P2₁/c*) from powder diffraction data with standard crystallographic methods provides a clear demonstration of the power of the new texture approach. This is by far the largest structure solved directly from powder diffraction data to date. The method has the advantage that prior chemical knowledge (other than chemical composition) is not required for the structure determination, so the solution is not biased by any assumptions about the structure. The extracted diffraction intensities are sufficiently single-crystal-like to allow even very large structures to be solved with conventional methods.

The framework topology of UTD-1F (structure type code **DON**) that emerged from this structure determination can be described in terms of layers of “butterfly” units (a 6-ring “body” with two 5-rings on each side forming the “wings”) arranged in a centered manner (see Figure 4). The 5-rings of these units are linked via oxygen bridges to the 5-rings of the four neighboring units to form 4-rings and oval 14-rings with a free aperture of ca. 8×10 Å. Adjacent layers are mirror images of one another. A strict UD (up–down) alternation of the orienta-

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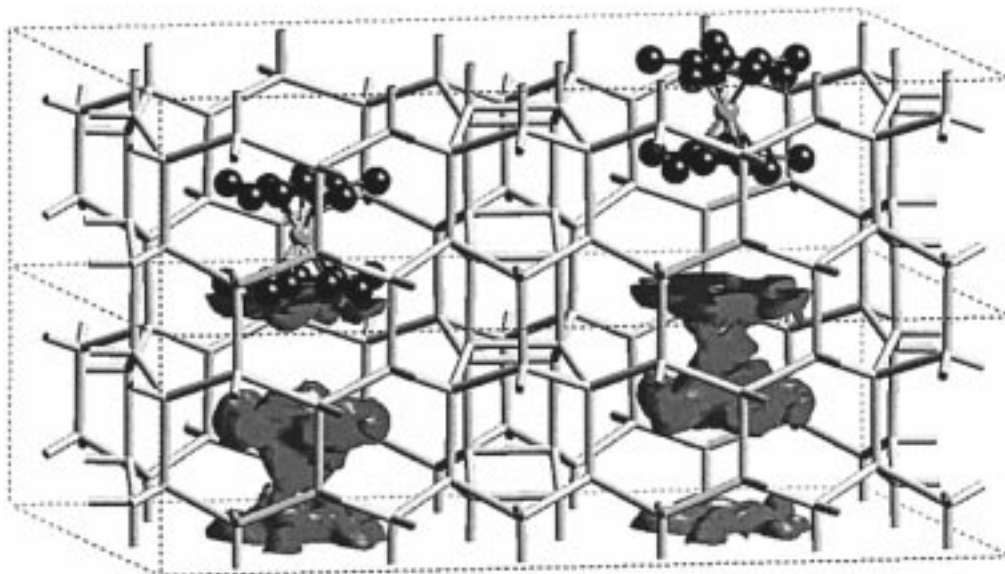


Figure 5. Arrangement of the $(\text{Cp}^*)_2\text{Co}$ complexes in the 14-ring channels of UTD-1F. The difference electron density map generated in *Pc* with the atoms of the framework and the Co position as the structural model is shown in the lower unit cell, and the final structure in the upper one.

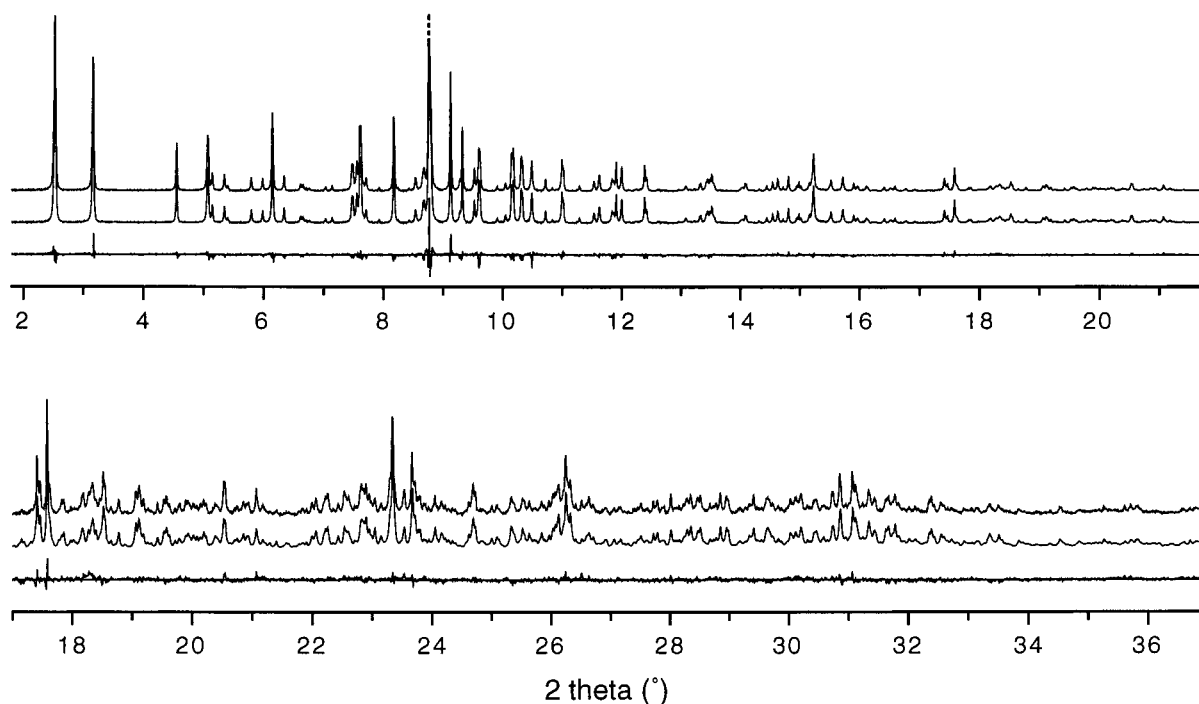


Figure 6. The observed (top), calculated (middle), and difference (bottom) profiles for the Rietveld refinement of UTD-1F. To show more detail, the highest peak has been cut at approximately 60% of its full height, and the intensity scale for the second 2θ range has been increased by a factor of 5.

tion of the Si tetrahedra in the 14-rings creates a channel wall consisting of 6-rings only (see Figure 5). The 4-rings have an UDD arrangement of Si tetrahedra, and form double crankshafts between parallel 14-ring channels. A comparison of this framework topology with the polymorphs described by Lobo and co-workers⁶ shows it to be that of their polymorph C. However, the framework structure of UTD-1F has a much lower symmetry than does the ideal topology (which only describes the connectivity of the tetrahedral atoms in the highest possible symmetry). The two types of 14-rings along the channel, for example, are not related by symmetry in UTD-1F.

As predicted by Lobo et al.,⁶ the organometallic complex orients itself in the 14-ring channel. The electron density map and subsequent successful refinement clearly show that the

$[(\text{Cp}^*)_2\text{Co}]^+$ ion is oriented with its 5-fold axis parallel to the channel direction (Figure 5). The Co lies in the plane of one of the two symmetrically independent 14-rings with the Cp^* rings lying above and below it (between adjacent 14-rings). This arrangement allows almost all short distances between the methyl groups of the Cp^* rings and the oxygens of the framework to be avoided. However, the oval shape of the 14-rings, the small displacement of the organometallic complex from the center, and the 5-fold point symmetry of the complex, which is not compatible with that of a 14-ring, lead to one short $\text{C}(\text{Me})\text{--O}$ distance of 2.93(7) Å [$\text{C}(10)\text{--O}(5)$]. All other $\text{C}(\text{Me})\text{--O}$ distances have reasonable values between 3.3 and 3.9 Å. This observation may be real, but may also be an artifact. With so many parameters, the precision of the atomic coordi-

nates is too low to allow a detailed interpretation. The Co complexes in adjacent channels along the *c* direction are related by the *c*-glide plane and alternate in height ($y \approx 3/4$ and $y \approx 1/4$), while those along the *a* direction are related by translation and are therefore at the same height. This arrangement of the nonframework species is probably the primary cause of the monoclinic distortion of the structure.

Small distortions of the framework and the ordering of the $[(\text{Cp}^*)_2\text{Co}]^+$ ions described above cause the ideally B-centered orthorhombic framework to become primitive monoclinic. The relationship between the two unit cells is shown in Figure 4. The "orthorhombic" setting of the unit cell for UTD-1F has the dimensions $a = 18.736 \text{ \AA}$, $b = 8.470 \text{ \AA}$, $c = 23.414 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90.2^\circ$, and $\gamma = 90^\circ$ (compared with $a = 18.98 \text{ \AA}$, $b = 8.41 \text{ \AA}$, $c = 23.04 \text{ \AA}$, and $\alpha = \beta = \gamma = 90^\circ$ for calcined UTD-1⁶). The deviation from an orthorhombic metric is quite small, but the symmetry is clearly monoclinic. Closer inspection of the shapes of the 14-rings shows that the one with the Co in the center is more circular than the one without. The major and minor axes of the free aperture of the former are 10.09 and 7.91 \AA , while those of the latter are 10.33 and 7.85 \AA . In contrast to the structure analysis of calcined UTD-1 reported by Lobo et al.,⁶ this refinement clearly shows that there is no significant disorder or faulting in the UTD-1F framework.

Although the results of both the ^{19}F MAS NMR and chemical analysis indicate that F^- is present in the sample, it could not be located in the structure analysis. The ^{19}F MAS NMR spectrum is very similar to that found by Koller and co-workers for ZSM-5 prepared in fluoride medium.⁹ Investigations of several high-silica zeolite systems by that group have shown that the F^- ions are coordinated to Si in the framework to form 5-coordinate Si atoms. In the case of ZSM-5 at room temperature, the fluoride ions exchange between several Si sites, and only at 140 K do they "freeze out". It is quite conceivable that the situation is similar in UTD-1F, and that the 1.5 F^- ions per unit cell could not be located because they are disordered over several positions at room temperature. The ^{29}Si MAS NMR of UTD-1F shows a broad band of unresolved signals in the range 104–117 ppm corresponding to tetrahedrally coordinated Si. No obvious peak indicative of the presence of 5-coordinate Si is apparent, but with only 0.75 F per 32 Si it would be very weak and not easy to detect. The corresponding peak for ZSM-5 is very broad at room temperature.¹⁵

The topology of the UTD-1F framework proved to be the same as that of one of the polymorphs used to describe calcined UTD-1,⁶ so a comparison of the diffraction pattern of UTD-1F

with that of the as-synthesized form of UTD-1 prepared without fluoride was of interest. For this purpose, synchrotron powder diffraction data collected on conventionally prepared UTD-1 were kindly provided by Prof. Raul Lobo and Dr. Ron Medrud. Comparison of the two patterns showed that while they have some obvious similarities, there are also a number of differences. In particular, the positions of the peaks show that the unit cell dimensions are significantly different, and the pattern for UTD-1F has many more peaks. An approximate correspondence in the general trend of the diffracted intensities is apparent, but there are considerable variations in individual reflection intensities.

Conclusions

The combination of a synthesis in fluoride medium, a new texture method for structure determination, and high-resolution synchrotron powder diffraction data has allowed the very complex structure of UTD-1F to be determined and refined. The optimized synthesis procedure produced a highly crystalline sample of a fully ordered form of UTD-1 (polymorph C in ref 6). Not only is no stacking disorder apparent in the framework structure itself, but the $[(\text{Cp}^*)_2\text{Co}]^+$ ion in the 14-ring channels is also arranged in an ordered fashion. The Co complex is oriented with its 5-fold axis parallel to the channel direction, and the Co is located in the plane of alternate 14-rings along the channel. The fluoride counterion is probably disordered over several sites, and could not be located. Despite the size of the structure (117 non-H atoms in the asymmetric unit), Rietveld refinement was stable and produced a chemically sensible result. It appears that the limits of the Rietveld method can be expanded when the data are of such high quality.

Acknowledgment. We thank the SNBL for allowing us access to their synchrotron facility and Dr. P. Pattison, W. van Beek, and S. Brenner for their assistance with the synchrotron data collections. We also thank Prof. H. Kessler, Université de Haute Alsace, Mulhouse for the ^{19}F and ^{29}Si MAS NMR spectra, Mr. P. H. M. Corbet, Shell Research and Technology Center, for the SEM analysis, and Prof. R. Lobo, University of Delaware, and Dr. R. Medrud, Chevron Research and Technology, Richmond, CA, for sharing their (unpublished) synchrotron powder diffraction data for as-synthesized UTD-1 with us. This work was supported by the Swiss National Science Foundation.

Supporting Information Available: Tables of crystal data and atomic coordinates and displacement parameters for UTD-1F (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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