SSZ-23: An Odd Zeolite with Pore Openings of Seven and Nine Tetrahedral Atoms**

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Millions of years of nature and four decades of synthetic effort have resulted in more than sixty known thermally stable aluminosilicate zeolites.[1] Their ordered microporous architecture enables small molecules to be discriminated on the basis of their size and shape: a property that is used extensively in separation processes and catalysis. We have found that SSZ-23 is the first aluminosilicate zeolite to possess pores bounded by nine tetrahedral atoms. This surprising result fundamentally alters the expected shape-selective influence in molecular sieving and hydrocarbon transformations, which unleashes great potential for new and improved separation and catalytic processes.

Solid-state chemists describe inorganic oxides consisting of infinite ionic arrays in terms of constituent building units: tetrahedra, octahedra, chains, rings, sheets, and blocks. This not only permits rationalization of their structural chemistry but also acts as a spur for the synthesis of new materials that may have related but distinct architectures and composition and, as a result, different and desirable properties. Microporous framework solids exhibit a particularly rich diversity of structure and applications, and each discovery of a novel material provides fresh insight, revealing a predicted (but until then unobserved) member of a structural series or a framework with completely new and unexpected features. Recent examples in the latter category include the aluminophosphate VPI-5 with a pore constrained by a ring of eighteen tetrahedra (eighteen-membered ring, 18MR),[2] aluminosilicates with interconnected channels bound by both 10MRs and 12MRs,[3] and aluminosilicates with two independent multidimensional channel systems[4] or with pore openings bounded by 14MRs.[5] Each new example has stimulated great interest because of the promise it holds for improved catalytic and molecular sieving properties. The group of Zones at Chevron has been particularly active during this period in the synthesis of new zeolites by use of custom-made, structure-directing templates.

Among the wealth of new materials discovered, the zeolite SSZ-23, patented in 1987, was found to have catalytic properties for the reaction of methanol to hydrocarbons that correspond to those of a medium-pore zeolite.[6] Conventional wisdom suggested that it must have channel openings to the internal acid sites bounded by 10MRs (rather than 8MR or 12MRs, the other possible pore openings), but because of the small crystallite size, structure solution was not possible. We will show that SSZ-23 is, in fact, the first aluminosilicate with 9MR pore openings, and the first microporous solid to contain both 7MR and 9MR openings—in this respect it is truly an odd zeolite.

Our unexpected discovery was made possible by the rapid development of the extremely powerful field of microcrystalline X-ray diffraction (diffraction on very small single crystals) accomplished at synchrotron radiation sources. For reasons of crystallographic complexity, it is unlikely that the structure could have been solved in any other way. The power of this crystallographic method is such that the position of the organic template cation was revealed, showing that its orientation alternates in adjacent cages. Not only does our study explain the observed catalytic and sorption behavior, but a whole new range of structural possibilities for aluminosilicates is suggested, as yet unconsidered because of preconceptions of the expected building blocks. Now that 9MRs have been observed in thermally stable and strongly acidic solids, new catalytic applications will certainly follow.

Initially, a sample of aluminosilicate SSZ-23 was prepared according to published methods as a very fine microcrystalline powder, and was found to have a powder X-ray diffraction pattern as reported in the literature.[6] In separate experiments, pure silica SSZ-23 was synthesized at near neutral pH with *N,N,N*-trimethyl-1-adamantammonium ($TMAda^+$) cations as structure-directing agents and F^- anions as mineralizers. Chemical analysis suggests the following formula for the unit cell: $[(C_{13}H_{24}N^+)_{4.1}F^-_{3.3}(OH)_{0.8}(H_2O)_{1.6}][SiO_2]_{64}$ (found: N 1.20, C 13.50, H 2.16, F 1.31; calculated for $[C_{13}H_{24}N^+F^-(H_2O)_{0.5}]_4[SiO_2]_{64}$ N 1.19, C 13.24, H 2.14, F 1.61). The weight loss up to 800°C was 19.7% instead of the calculated 18.8%. Thus, F^- ions seem to be present in slightly smaller concentrations than required to balance the positive charge of the organic cation. In the above experimental formula we have included OH^- to achieve charge balance. However, in view of the ^{29}Si MAS NMR spectrum, it appears more realistic to consider the presence of a small amount (2.7%) of connectivity defects in the form of $SiOH/SiO^-$ couples (which gives the required 0.8 additional negative charges per unit cell). The zeolite was stable during thermal removal of the template in air, and N_2 adsorption isotherms at

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77 K of calcined SSZ-23 reveal a microporous volume of 0.20 $cm^3 g^{-}$(by the *T*-plot method; 0.226 as measured at $p/p_0 =$ 0.30). The Horvath – Kawazoe formalism[7] applied to the Ar isotherm at 87.3 K gives an average micropore diameter of 5.7 Å.

Attempts to solve the structure from high-quality synchrotron X-ray powder diffraction data with simulated annealing and Monte Carlo computational techniques were all unsuccessful. Small crystals of SSZ-23 were then examined at the Synchrotron Radiation Source, Daresbury (UK). The need to use synchrotron X-ray radiation for this study is demonstrated by the recent work of Zones and co-workers, in which a SSZ-42 zeolite crystal of four times the volume of the SSZ-23 crystal produced data that was too weak, when collected on a similar instrument in the laboratory, to yield a refined structural model of suitable quality.[8]

In broad structural terms, the tetrahedral framework of SSZ-23 can be thought of as two-dimensional arrays of cages, with molecular access between the cages in the planes of the arrays restricted by the 7MR and 9MR pore openings. A more detailed structural consideration shows that the smallest characteristic subunit of SSZ-23 consists of three 4MRs and four 5MRs (Figure 1). These are linked together, through

Figure 1. Two of the characteristic subunits of SSZ-23 (see text for further details). The diagram also shows the location of the partially occupied fluorine sites inside the small cages. Si atoms are shown as grey spheres, O atoms as clear spheres, and F atoms as black spheres.

4MRs and 6MRs, to form slightly puckered layers parallel to the (101) face of the unit cell. These layers are then linked together by 4MRs to give the three-dimensional structure shown in Figure 2. This "pillaring" of layers produces channels running parallel to the [001] direction that are bounded at their narrowest points by 7MR windows. Parallel to the [101] direction are the channels bounded by 9MR windows, slightly offset against each other (Figures 3 and 4). Cages are located at the intersection of the 7MR and 9MR channels. The $TMAda^+$ template cations inside the cages were located by difference Fourier techniques (Figure 5).

Unusually for zeolites, the cages have no symmetry; the template molecules are aligned parallel to the long axis of the cages. Careful examination of the difference Fourier map

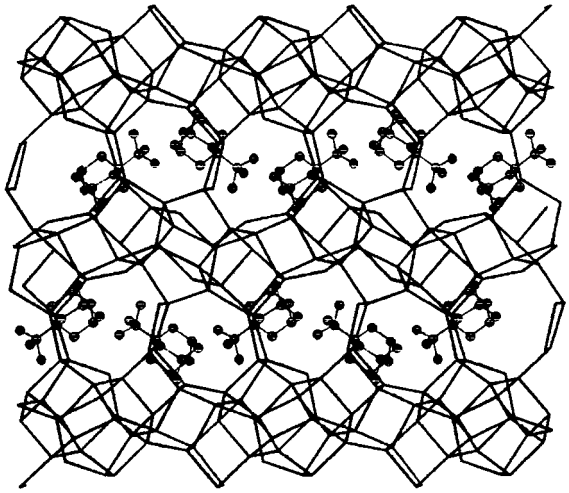

Figure 2. The structure of SSZ-23 viewed parallel to the [001] direction, showing the 7MR windows and the orientation of the $TMAda^+$ cation. For clarity, the framework structure is shown as single lines joining the Si atoms; O atoms, which would be placed near the centers of the lines, have been omitted.

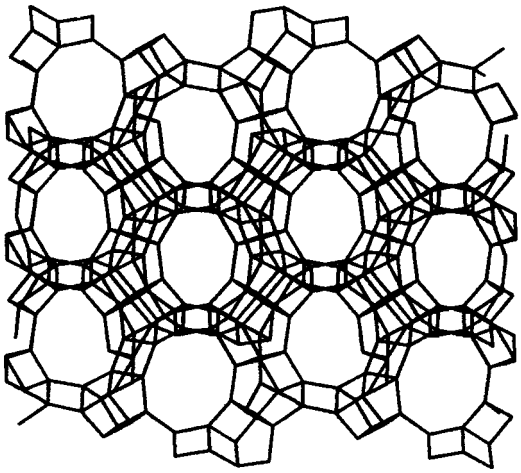

Figure 3. The framework structure of SSZ-23 viewed parallel to the [101] direction, showing the channels bounded by the 9MR windows. For clarity, the template molecule has been omitted and the framework is depicted in the same fashion as in Figure 2.

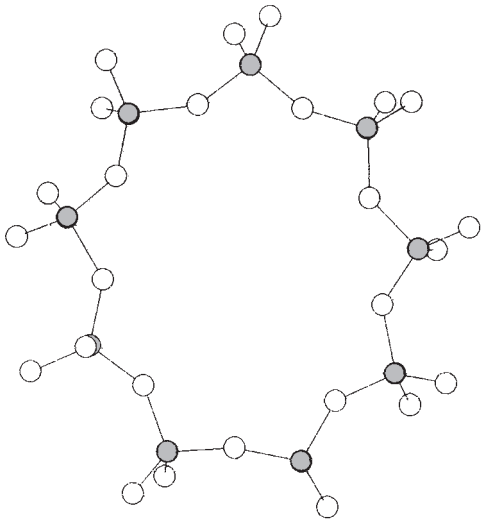

Figure 4. Detail of one of the 9MRs from SSZ-23. The Si atoms are depicted as grey spheres, and the O atoms as white spheres.

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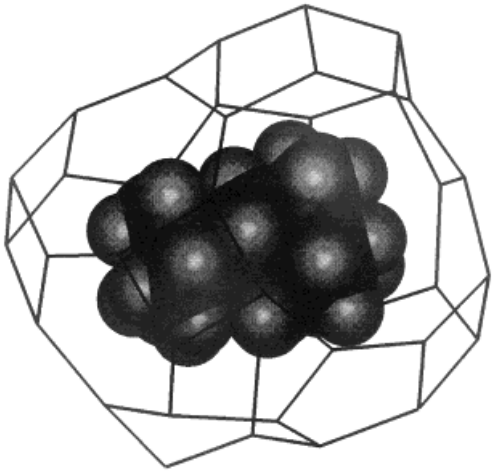

Figure 5. The $TMAda^+$ templating cation, depicted as a space-filling model, inside the cage formed by the intersection of the 9MR and 7MR channels.

revealed three regions of residual electron density within the small structural subunits shown in Figure 1. These are attributed to the charge-balancing fluoride ions detected in the chemical analysis. They are bonded to silicon atoms, increasing the silicon coordination to fivefold with bond lengths (Si(7)–F(3) 1.96(3), Si(12)–F(1) 1.937(14), Si(13)–F(2) 1.95(2) Å) that are consistent with both the ^{29}Si MAS NMR spectra and other reports of fluoride-containing zeolites and silica polymorphs for which a preference for the F^- ions to reside in small cages has been seen. The total refined occupancy of the three F^- ion sites is also in reasonable agreement with the expected value from the chemical analysis. A preliminary Rietveld refinement of our structural model against powder X-ray diffraction data from the aluminosilicate SSZ-23 sample confirms that the framework structures of the two materials are identical.

The ^{29}Si MAS NMR spectrum of the as-synthesized material consists of two very broad bands ($\delta \approx -108$ and -114; Figure 6). Both bands can be assigned to Si(4Si) sites, and show some resolution of crystallographically independent sites. In fact, a simulation of the spectrum using the Si-O-Si angles derived in this work and the equation of Thomas et al.[9] and neglecting the influence of F^- gives the same two broad bands with about the same intensities when pure Gaussian lines with full width at half maxima of 2 ppm are used. The low resolution of this spectrum is probably a consequence of considerable line broadening due to heteronuclear coupling of ^{29}Si with ^{1}H and ^{19}F nuclei. In this spectrum there is also a broad shoulder at $\delta \approx -102$ (2.7% relative intensity) and a very broad hump in the region $\delta = -130$ to -150 (4% relative intensity). The former is probably due to the presence of a very small number of connectivity defects, in agreement with the lower than expected F^- ion content. The latter appears in the region expected for pentacoordinated Si atoms: SiO_4F units in the clathrasil framework structure nonasil (NON)[10] resonate at about $\delta = -144$ (Si–F ca. 1.8–1.9 Å), while in TPAF-silicalite a broad hump very similar to the one shown here appears in the region $\delta = -115$ to -135.[11] This feature has been assigned to pentacoordinated Si atoms bonded to F^- ions that rapidly exchange at room temperature between different Si sites. Our ^{29}Si NMR spectra and X-ray diffraction results seem to confirm this assignment.

The ^{29}Si NMR spectrum of the calcined material shows enhanced resolution, and no resonances around $\delta = -100$ that could be assigned to SiOH connectivity defects, which indicates that they are annealed upon heating. There is also no evidence of pentacoordinated Si atoms, which indicates that the F^- ions leave the material, probably as HF, during calcination. All resonances appear in the Si(4Si) region and, despite a significant overlap of the peaks, at least nine different sites (seven lines plus two shoulders) can be distinguished. The resolution of crystallographic sites is a consequence of the lack of connectivity defects, the high degree of local order of the material, and the absence of heteronuclear coupling of ^{29}Si with ^{1}H or ^{19}F nuclei. By the use of the equation of Thomas et al.,[9] the average Si-O-Si angle for every Si site is shown to fall in the range of 140.8 to 159.8°. Furthermore, the experimental ^{29}Si MAS NMR spectrum is in reasonable agreement with the spectrum calculated from the values obtained from a preliminary Rietveld refinement of the powder diffraction data of the calcined material.

The SSZ-23 structure type is an intriguing addition to the family of high-silica zeolites, and can be prepared with or without aluminium in the framework. Light is shed on the role of fluoride as a mineralizer in silicate crystallization by its inclusion in the framework structure attached to pentacoordinated silicon atoms. The presence of 7MRs and 9MRs in a stable solid acid is unexpected. Among the known zeolite topologies, rings with an odd number of tetrahedra are rare (with the exception of the more frequent 5MR), while even-numbered rings are ubiquitous (4MR, 6MR, 8MR, 10MR,

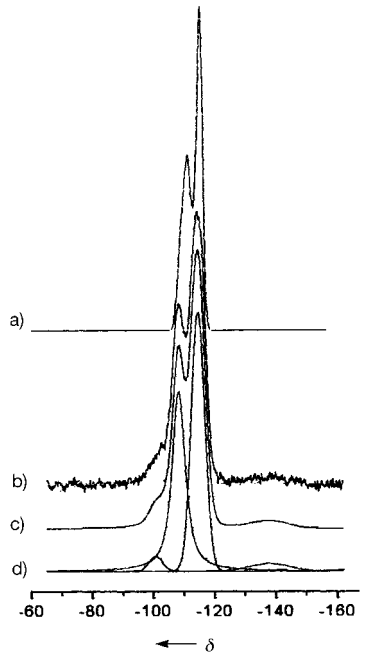

Figure 6. ^{29}Si MAS NMR spectra of as-synthesized SSZ-23: a) Simulation using the Si-O-Si angles obtained in this work and the equation of Thomas et al.[9] b) Experimental spectrum. c) Simulation with all deconvoluted components. d) Individual deconvoluted components.

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Table 1. Fractional coordinates and equivalent isotropic displacement parameters U_{equiv} for SSZ-23.[a]

Atom	x	y	z	U_{equiv} [Å^2]	Atom	x	y	z	$U_{eq.}$ [Å^2]
Si(1)	0.59105(15)	0.16686(9)	0.20389(14)	0.0097(4)	O(18)	0.6618(5)	0.1137(3)	0.1752(5)	0.0302(14)
Si(2)	0.6351(2)	0.16809(9)	0.44152(15)	0.0127(4)	O(19)	0.4741(4)	0.1588(2)	0.1421(4)	0.0230(13)
Si(3)	0.69632(15)	0.57232(9)	− 0.03740(15)	0.0107(4)	O(20)	0.5929(4)	0.3488(2)	0.4575(4)	0.0209(12)
Si(4)	0.66614(15)	0.49124(9)	0.13311(14)	0.0094(4)	O(21)	0.5313(4)	0.0435(3)	0.5938(4)	0.0231(13)
Si(5)	0.6625(2)	0.29875(9)	0.21813(15)	0.0112(4)	O(22)	0.2550(4)	0.4651(3)	0.4069(4)	0.0271(14)
Si(6)	0.6889(2)	0.30373(9)	0.44861(15)	0.0112(4)	O(23)	0.7727(4)	0.5288(3)	− 0.0852(5)	0.0308(15)
Si(7)	0.5039(2)	0.40460(10)	0.1951(2)	0.0148(4)	O(24)	0.6977(5)	0.5644(3)	0.4059(4)	0.0300(15)
Si(8)	0.4663(2)	0.09638(9)	0.52554(15)	0.0118(4)	O(25)	0.1585(5)	0.5697(2)	0.4003(4)	0.0263(13)
Si(9)	0.7777(2)	0.55142(9)	0.33339(15)	0.0117(4)	O(26)	0.7033(4)	0.2962(3)	0.3361(4)	0.0226(13)
Si(10)	0.36884(14)	0.00001(9)	0.37794(14)	0.0082(4)	O(27)	0.5580(4)	0.3389(2)	0.1887(4)	0.0208(12)
Si(11)	0.1541(2)	0.50214(9)	0.35464(14)	0.0119(4)	O(28)	0.8602(4)	0.4980(3)	0.3767(4)	0.0244(13)
Si(12)	0.8221(2)	0.38557(9)	0.1683(2)	0.0133(4)	O(29)	0.0522(5)	0.4660(3)	0.3707(5)	0.036(2)
Si(13)	0.5381(2)	0.41447(10)	0.4240(2)	0.0203(5)	O(30)	0.3415(5)	0.0086(3)	0.2609(4)	0.0292(14)
Si(14)	0.8892(2)	0.37328(9)	0.55406(15)	0.0108(4)	O(31)	0.7965(4)	0.3253(2)	0.5173(4)	0.0219(12)
Si(15)	0.3487(2)	0.46238(10)	0.5030(2)	0.0159(5)	O(32)	0.6054(4)	0.4709(3)	0.4705(5)	0.037(2)
Si(16)	0.9363(2)	0.44089(10)	0.3693(2)	0.0164(5)	N(1)	0.2428(8)	0.7703(5)	0.1550(11)	0.081(4)
O(1)	0.6380(4)	0.5326(2)	0.0329(4)	0.0136(11)	C(1)	0.3457(7)	0.7267(4)	0.1737(7)	0.034(2)
O(2)	0.5926(4)	0.1660(3)	0.3221(4)	0.0242(13)	C(2)	0.5292(15)	0.7219(12)	0.1601(26)	0.171(13)
O(3)	0.9008(5)	0.4015(3)	0.2708(4)	0.035(2)	C(3)	0.3687(15)	0.7103(9)	0.2776(11)	0.116(7)
O(4)	0.6618(4)	0.2360(2)	0.4841(4)	0.0190(12)	C(4)	0.4504(11)	0.6122(6)	0.2391(12)	0.078(4)
O(5)	0.5436(4)	0.1450(2)	0.4930(4)	0.0220(13)	C(5)	0.4773(16)	0.6709(7)	0.2948(12)	0.097(6)
O(6)	0.7546(4)	0.3237(2)	0.1668(4)	0.0179(12)	C(6)	0.2674(14)	0.8296(6)	0.2124(12)	0.105(6)
O(7)	0.7534(4)	0.4429(2)	0.1182(4)	0.0218(12)	C(7)	0.5595(13)	0.7035(8)	0.2696(20)	0.137(10)
O(8)	0.6365(4)	0.2305(2)	0.1751(4)	0.0157(11)	C(8)	0.3194(13)	0.6723(6)	0.1102(15)	0.130(9)
O(9)	0.4366(4)	0.4154(3)	0.4794(4)	0.0233(13)	C(9)	0.4313(10)	0.7629(7)	0.1453(15)	0.100(6)
O(10)	0.9431(4)	0.3958(3)	0.4641(4)	0.0204(12)	C(10)	0.4250(16)	0.6300(8)	0.1223(20)	0.149(12)
O(11)	0.3965(4)	0.1321(2)	0.5894(4)	0.0132(11)	C(11)	0.1602(12)	0.7437(10)	0.1979(23)	0.205(15)
O(12)	0.5605(4)	0.4591(2)	0.1489(4)	0.0208(12)	C(12)	0.5153(23)	0.6654(12)	0.1113(18)	0.158(13)
O(13)	0.6119(4)	0.6022(2)	− 0.1252(4)	0.0188(12)	C(13)	0.2111(18)	0.7845(10)	0.0455(15)	0.188(14)
O(14)	0.7357(4)	0.1251(3)	0.4725(4)	0.0260(13)	F(1)[b]	0.7395(11)	0.4040(7)	0.2683(10)	0.025
O(15)	0.4869(4)	0.4187(3)	0.3065(4)	0.0268(13)	F(2)[b]	0.6632(13)	0.4191(8)	0.3659(13)	0.025
O(16)	0.3942(4)	0.0661(2)	0.4285(4)	0.0187(12)	F(3)[b]	0.6473(27)	0.4140(16)	0.2743(26)	0.025
O(17)	0.7114(4)	0.5353(2)	0.2244(4)	0.0219(13)					

[a] Numbers in parentheses represent the estimated standard deviations on the last digit or digits. The fluorine displacement parameters are fixed. [b] The fluoride ion site occupancies, SOF, for F(1) – F(3) are 0.317(10), 0.262(10), and 0.131(10).

12MR).In the very few cases in which 3MRs, 7MRs, or 9MRs are known, their presence is associated with either Zn^{2+} or Be^{2+} sites in the tetrahedral building units or to a very specific templating effect. Thus, the LOV, VSV, and RSN structure types represent the only zeolite-type materials to possess a fully connected three-dimensional network of tetrahedra with 3MR and 9MRs, and all of them have Zn^{2+} or Be^{2+} sites in the structure.[1] On the other hand, ZSM-18 (MEI) is the only known zeolite with 7MRs.[12]

With our knowledge of the structural features, we can now explain previous catalytic studies that showed that SSZ-23 produced *para*-xylene selectively during the conversion of methanol into aromatic hydrocarbons.[6] The initial interpretation was that the structure possessed 10MR pore openings. In addition, adsorption data showed that *n*-hexane was adsorbed much more readily than 3-methylpentane and 2,2-dimethylbutane, in strong contrast to ZSM-5. With the knowledge of the structure, we see that these data are explained by the 9MR pore openings, which have free diameters of 5.4 × 3.8 Å. The 7MRs are considerably smaller, with free diameters of 3.5 × 2.5 Å. An immediate application of such 9MR zeolites would be in the isomerization of xylenes, because *para*-xylene is a mainstay of the fabric industry through its conversion into terephthalic acid. Further work is in progress to investigate further the shape-selective properties of 9MR structures. We also wish to emphasize that it is unlikely that any technique other than microcrystalline diffraction could have yielded the structure. The low symmetry and large unit cell result in sixteen tetrahedral cation sites in the asymmetric unit, making ab initio solution from powder data improbable. Moreover, the lack of a suitable projection axis means that high-resolution electron microscopy could not have yielded crucial information, and model building approaches would have been hampered by the absence of accepted secondary building units as starting points. Indeed, SSZ-23 had already remained unsolved for a decade before the advent of both improved synthetic methods using fluoride ions and the extremely powerful technique of microcrystalline diffraction.

Experimental Section

Synthesis of purely siliceous SSZ-23: Tetraethylorthosilicate (10.42 g) was hydrolyzed in an aqueous solution of TMAdaOH (32.56 g of a 0.767 M solution). The ethanol produced, together with some water, was allowed to evaporate completely (within the limit of detection of ^{1}H NMR spectroscopy) at room temperature under stirring. Then, HF (1.033 g, 48 % aq) diluted in water (0.91 g) was added, and the white slurry formed was placed into Teflon-lined 60-mL stainless steel autoclaves. The reaction mixture ($1.0\,SiO_2$:$0.50\,TMAdaOH$:$0.50\,HF$:$15\,H_2O$) was heated at 150 °C under rotation (60 r min^{-1}) for 30 d. The solid product was recovered by filtration (80 % yield, based on SiO_2), washed with distilled water, and dried at 100 °C.

Single-crystal X-ray diffraction: A small single fragment (20 × 20 × 5 μm^3) of a twinned crystal of pure silica SSZ-23 was used. X-ray diffraction data

were collected at 160 K with a Bruker AXS SMART CCD area-detector diffractometer on the high-flux single-crystal diffraction station 9.8 at CCLRC Daresbury Laboratory Synchrotron Radiation Source, with a wavelength of 0.6849 Å selected by a horizontally focusing silicon (111) monochromator and vertically focused by a cylindrically bent palladium-coated zerodur mirror.[13] The data set covered more than a hemisphere of reciprocal space with several series of exposures, each series with a different crystal orientation and each exposure taken over 0.2° rotation. Corrections were made for the decay of the synchrotron beam intensity as part of standard interframe scaling procedures.[14] The SSZ-23 sample was examined in the as-synthesized form and therefore included the template and charge-balancing fluoride ions. The crystal structure of SSZ-23 was solved with the direct methods program SHELXS-97[14] and refined with a full-matrix least-squares technique with the program SHELXL-97.[14] The final cycle of least-squares refinement included anisotropic displacement parameters for silicon, oxygen, carbon, and nitrogen atoms, and fractional occupancies for the fluorine atoms. The hydrogen atoms of the template molecule were placed in chemically sensible positions, and their positions were recalculated after each cycle of refinement. A total of 22014 integrated intensities were measured ($1.79 < \theta < 28.27°$), of which 8314 were unique and 4665 observed ($F^2 > 2\sigma(F^2)$). The large proportion of unobserved reflections is due to the small size of the crystal. Final refinement of the 571 least-squares parameters converged to $wR(F^2_{obs.}) = 0.1657$, $wR(F^2_{all\ data}) = 0.2028$, $R(F_{obs.}) = 0.0811$, $S(F^2_{all\ data}) = 0.992$; max. residual electron density = 0.744 e Å^{-3}. Refinement on F^2 was carried out against all data; the observed criterion $F^2 > 2\sigma(F^2)$ was used only for the calculation of $wR(F^2_{obs.})$ and $R(F_{obs.})$ and is not relevant to the choice of reflections for refinement. The final unit cell was refined to $a = 12.9594(3)$, $b = 21.7919(6)$, $c = 13.5980(4)$ Å, and $\beta = 101.855(2)°$, $V = 3758.3(2)$ Å at $T = 160$ K, space group $P2_1/n$, $\rho_{calcd} = 2.13$ g cm^{-3}. Details of the final atomic coordinates, equivalent isotropic displacement parameters, and fluoride ion occupancies are given in Table 1. Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-408348.

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Formation of Isomeric Tetrathiotungstate Clusters [{Cp*Ru(CO)}$_2$(WS$_4$){W(CO)$_4$}] by the Reaction of [Cp$^*_2$Ru$_2$S$_4$] with [W(CO)$_3$(MeCN)$_3$]

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Dinuclear transition metal sulfur complexes of the type [Cp$^*_2$M$_2$S$_4$] (Cp* = η^5-C$_5$Me$_5$) are excellent starting materials for the formation of multinuclear transition metal sulfur clusters.[1] However, surprisingly little is known about reactivity of the iron-[2] or ruthenium-containing complexes.[3] In 1994 our group reported the reactions of [Cp$^*_2$Fe$_2$S$_4$] with iron and ruthenium carbonyl complexes to give *closo*-[Cp$^*_2$(CO)$_3$Fe$_2$MS$_2$] clusters (M = Fe, Ru).[2] Rauchfuss et al. reported that the ruthenium analogue [Cp$^*_2$Ru$_2$S$_4$][4] reacts with [Cp*Ru(MeCN)$_3$](PF$_6$) and [Cp*Rh(MeCN)$_3$](PF$_6$)$_2$ to give [Cp*$_3$Ru$_3$S$_4$](PF$_6$)[3a] and [Cp*$_3$RhRu$_2$S$_4$(MeCN)](PF$_6$)$_2$,[3c] respectively. To examine whether this cluster construction methodology can be applied generally, the thermal reaction of [Cp$^*_2$Ru$_2$S$_4$] with [W(CO)$_3$(MeCN)$_3$] was investigated, and is described here. In the reaction, there was a dramatic redistribution of CO and S ligands between the W and Ru centers to give geometric isomers of tetrathiotungstate clusters [{Cp*Ru(CO)}$_2$(WS$_4$){W(CO)$_4$}]. Furthermore, we observed thermal and photochemical interconversion between the two isomers.

A solution of [Cp$^*_2$Ru$_2$S$_4$] in toluene was added to a solution of [W(CO)$_3$(MeCN)$_3$][5] (2 equiv) in acetonitrile (Scheme 1). The mixture was heated at 50 °C with stirring for 40 minutes. Evaporation of the volatile components and subsequent flash chromatographic separation of the residue over silica gel gave the two red-brown clusters **1** and **2** in 58% and 11% yield. Elemental analysis and mass spectrometry data indicated that **1** and **2** have the same formula Cp$^*_2$Ru$_2$W$_2$S$_4$(CO)$_6$,[6] which is consistent with a cubane-type mixed metal – sulfur cluster [(Cp*Ru)$_2${W(CO)$_3$}$_2$(μ_3-S)$_4$]. However, X-ray diffraction study disclosed that this is not the case.[7] Cluster **1** was unequivocally determined to be [{Cp*Ru(CO)}$_2${W(μ_3-S)$_2$(μ_2-S)$_2$}{W(CO)$_4$}] (Figure 1). Interestingly, according to the crystal structure of **1**, redistribution of CO and S ligands

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