poly(3-alkylthiophenes), however, are much alike, with maxima at higher wavelength (520 nm), indicating a much larger conjugation length in the solid state.[8b] Recently, the third-order nonlinear optical susceptibilities of some of the oligomers have been measured in poled PMMA solutions, and in this case saturation sets in at 7–8 thiophene units, thus indicating the sensitivity of planarity of these oligomers to matrix composition.[8a]

Comprehensive studies on the properties of these undecithiophenes and lower homologues as well as a full account of the synthesis of all these oligothiophenes will be published elsewhere.[8,13]

In conclusion, two oligothiophenes of unprecedented length have been prepared through a solid route. Moreover, these undecithiophenes bridge the gap that exists between the well-characterized lower oligothiophenes (up to sexithiophene) and the vaguely characterized polythiophenes.

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(13) Ten Hoeve, W.; Wynberg, H., to be published.

Aluminum and Gallium Oxide Pillared MoO_3

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It has been shown that microporous or zeolite-like structures can be constructed by intercalating large clusters between the layers of two-dimensional structures. These "pillaring" reactions were first reported for aluminosilicate clays.[1] They have not been extended to many simple transition-metal oxide hosts, other than titanium,[2] due to the difficulty in opening up the layers sufficiently to allow introduction of a large guest species. There is obvious interest in this approach as a route to developing and/or modifying metal oxides with specific properties. MoO_3, in particular, is a multifunctional material which has attracted considerable attention as a partial methane oxidation catalyst[3] and as a potentially viable cathode in secondary batteries.[4] The search for other polytypes of the layered structure of α-MoO_3 has led to two new phases,[5,6] but neither are microporous. We report here the first examples of pillaring of α-MoO_3 by the incorporation of $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ ("Al_{13}") to give rise to a microporous molybdenum oxide with a high surface area. The layers have also been pillared with a new oxy–gallium cluster which is analogous to the Al_{13} oligomer. Remarkably well-ordered materials are obtained which enables the first direct determination of the orientation of the guest Al_{13} cluster by 1-D Fourier analysis.

We prepared our pillared compounds by combining a solution of the guest cation species with a dispersion of the alkali-layered oxide. $Na_xMoO_3(H_2O)_y$ or $Li_xMoO_3(H_2O)_y$[7] was colloidally dispersed in water. We find that Li_xMoO_3 ($x = 0.25$) spontaneously exfoliates in water to give very stable dispersions of the MoO_3^{x-} layers. The layers are then are reassembled with inclusion of the pillars. This restructuring method was first demonstrated in the pillaring of TaS_2[8] with $Fe_6S_8(PEt_3)_6^{2+}$ and has recently been used to intercalate organic molecules in MoS_2.[9] The sodium compound also forms a dispersion, but our observations and recent TEM studies indicate that extensive exfoliation does not occur. This is in accordance with the lower solvation energy of the sodium cation compared to lithium. However, we find that Na_xMoO_3 undergoes sufficient swelling to permit direct exchange of the Na^+ for the polyoxycation. Solutions containing the pillaring agents were prepared by OH^- hydrolysis of $AlCl_3$[10] or $Ga(NO_3)_3$ solutions.

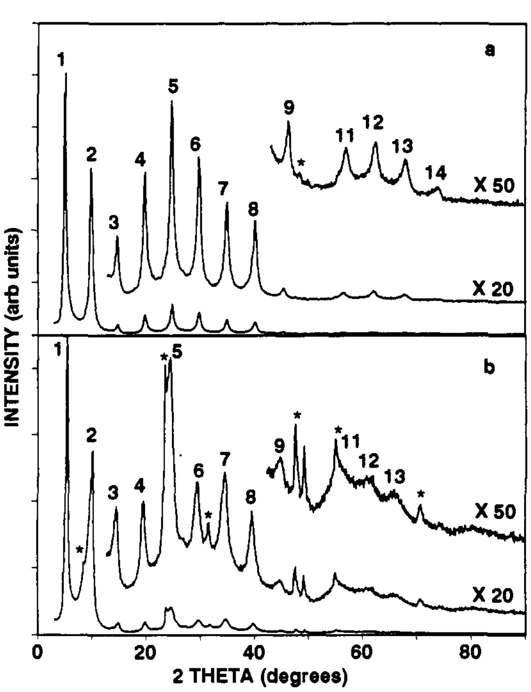

Figure 1. X-ray diffraction pattern (Cu Ka radiation) of oriented films of (a) $[(Al_{13})_{0.047}(Na)_{0.003}]MoO_3$ and (b) the 18-Å phase of gallium-pillared MoO_3 "$[(Ga_{13})_{0.032}(Na)_{0.09}]MoO_3$". Reflections arising from residual $[Na(H_2O)_2]_{0.25}MoO_3$ ($d_{0k0} = 11.39$ Å)[7] are marked with an (*). The intensity has been expanded by a factor of 20 and 50 in the upper traces in the figures; the integers indicate the ($0k0$) indices.

The X-ray diffraction pattern of the oriented thin film obtained from a Na_xMoO_3 dispersion flocculated with Al_{13} is shown in Figure 1a. The Li_xMoO_3-derived pattern was very similar. An average d spacing of 17.94 Å was calculated from the 14 $0k0$ ($00l$) reflections. The large number of reflections, together with the small variation in their d_{0k0} value (±0.03 Å) indicates that there is a high degree of order along the axis perpendicular to the layers. The interlayer expansion of 10.8 Å on pillaring is consistent with that observed for intercalation of Al_{13} in smectite clays (9.6 Å)[1] and also corresponds to the van der Waals diameter of Al_{13} (~10.5 Å). The degree of expansion is, to a certain extent, dependent on the topology of the layered surface and on the siting of the Al_{13} cations in the interlamellar gap. Chemical (Al, Mo, Na) and thermal gravimetric analysis of the as-prepared material gave the composition $[(Al_{13})_{0.047}(Na)_{0.003}(H_2O)_{1.0}]MoO_3$, showing that virtually complete ion exchange of the interlayer alkali cations has occurred. The films were extremely stable, showing no change in the XRD pattern after several days at ambient conditions. Drying the films in air at 100 °C for 2 days resulted in a decrease in the d spacing to 17.35 Å (14 sharp $0k0$ reflections, as before). Calcination at higher temperatures shows that a layered structure ($d = 15.2$ Å) is still present up to 350–400 °C but that interlayer collapse begins to occur at higher temperatures. The surface area [BET (N_2)] of the calcined material (200–250 °C) was 107 m^2/g. The surface area of the unpillared material (5 m^2/g) was negligible by comparison. Analysis of the pore size distribution showed that both micro and meso pores were present, with the surface area

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(1) Vaughan, D. E. W.; Lussier, R. J.; Magee, J. S. U.S. Patent 4,176,090, 1979. Pinnavaia, T. J.; Tzou, M. S.; Landau, S. D.; Raythatha, R. H. *J. Mol. Catal.* **1984**, *27*, 195.

(2) Cheng, S.; Wang, T.-C. *Inorg. Chem.* **1989**, *28*, 1283. Anderson, M. W.; Klinowski, J. *Inorg. Chem.* **1990**, *29*, 3260.

(3) Ono, T.; Kamisaki, H.; Hasashi, H.; Hiyata, H. *J. Catal.* **1989**, *116*, 303.

(4) Kumagai, N.; Tanno, K. *J. Appl. Electrochem.* **1988**, *18*, 857.

(5) McCarron III, E. M. *J. Chem. Soc., Chem. Commun.* **1986**, 336.

(6) Caiger, N. A.; Crouch-Baker, S.; Dickens, P. G.; James, G. S. *J. Solid State Chem.* **1987**, *67*, 369.

(7) Thomas, D.; McCarron III, E. M. *Mat. Res. Bull.* **1986**, *21*, 945. Also, see: Iwamoto, T.; Itoh, Y.; Ohwaka, K.; Takashi, M. *Nippon Kagaku Kaishi* **1983**, *2*, 273.

(8) Nazar, L. F.; Jacobson, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 570.

(9) Divigalpitya, W. M. R.; Frindt, R. F.; Morrison, S. R. *Science* **1989**, *246*, 369.

(10) Akitt, J. W.; Farthing, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1617.

0002-7863/91/1513-5889$02.50/0

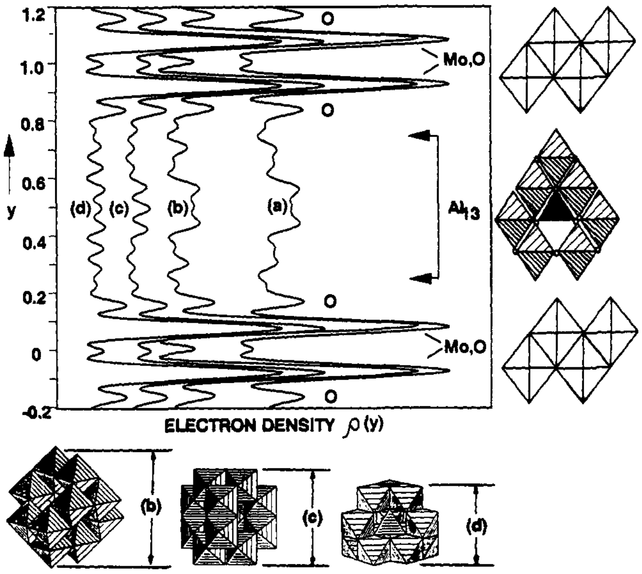

Figure 2. (a) Projection of the electron density of $[(Al_{13})_{0.047}(Na)_{0.003}(H_2O)_{1.0}]MoO_3$ along the interlayer axis, *y*. The scattering contributions from the lattice components are indicated on the figure. A schematic representation of the orientation of the Al_{13} cluster between the MoO_3 layers is shown on the right; (b) calculated projection with the C_2 axis of Al_{13} perpendicular to the layers, shown in (b) on the bottom; (c) calculated projection with the C_4 axis perpendicular to the layers, shown in (c) on the bottom; (d) calculated projection with the C_3 axis perpendicular to the layers, shown in (d) on the bottom.

contribution from each being roughly equal. The meso pores had a very narrow pore size distribution centered at a radius of 20 Å.

The "one-dimensional crystal structure" can be determined by 1-D electron density mapping. The Fourier transform of the structure factors obtained from the integrated X-ray intensities shown in Figure 1 resulted in the projection of the electron density along the interlayer axis shown in Figure 2a. Comparison with the calculated 1-D profiles for the Al_{13} in three different orientations (Figure 2b–d) shows that the Al_{13} cation is situated with the C_2 axis perpendicular to the layers. This may be responsible for the slightly larger interlayer expansion observed here, in comparison with that reported for clay minerals in which it is thought that the Al_{13} is oriented with the C_3 axis perpendicular to the layers.[1]

Treatment of the Li_xMoO_3 or Na_xMoO_3 dispersion with a Na-free, concentrated Ga–polyoxy cation solution resulted in a material which gave rise to a very similar diffraction pattern (d_{0k0} = 18.1 Å), Figure 1b, as that obtained for Al_{13}. ^{71}Ga NMR spectra of the hydrolyzed solutions showed that the NMR spectrum at 80 °C was similar to that of Al_{13};[10] namely, a single, narrow tetrahedral-site resonance was observed at 173.2 ppm (downfield from $Ga(H_2O)_6^{3+}$), with a very broad octahedral resonance barely visible at about 35 ppm. This, together with the almost identical values of interlayer expansion in the MoO_3 lattice, implies that the structure or composition of the Ga–polyoxy cation is very similar to Al_{13}.[11] After the initial submission of this paper, another report has appeared on the incorporation of a similar gallium species in clays, whose authors come to the same conclusion.[12]

Flocculation of the A_xMoO_3 with more dilute Ga–polyoxy cation solutions containing Na^+ (or dilute Al_{13} solutions) led to materials which also showed a very well-ordered diffraction pattern but which had an interlayer spacing of 25 Å. These were unstable, converting to a mixture of an 18 Å phase and A_xMoO_3 after a few hours. This suggests that they are due to a "alternate-stage" intercalation compound, in which an approximately 11-Å polyoxy cation is intercalated between every other MoO_3 layer. The intervening layers are occupied by either A^+ (A = Na, Li) or H^+. Such compounds have been observed under certain conditions for Al_{13} intercalated in montmorillonite clays.[13]

We have also been successful in forming pillared MoO_3 with other polyoxy cation clusters of Ti, Zr, and Cr.[14] The properties and thermal evolution of these materials will the subject of future investigations.

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Supplementary Material Available: Table I of XRD data for the 18-Å phase of $[(Al_{13})_{0.047}(Na)_{0.003}]MoO_3$ and the 25-Å phase of the Al_{13}-pillared MoO_3 and Table II of XRD data for the 18- and 25-Å phases of Ga polyoxycation pillared MoO_3 (2 pages). Ordering information is given on any current masthead page.

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[11] Chemical analysis of the pillared material gave a Ga/Mo ratio of 0.41, yielding a formulation of $[(Ga_{13})_{0.032}(Na)_{0.09}]MoO_3$. Note that some (or all) of the Na is present in a second phase (see Figure 1b).

[12] Bradley, S. M.; Kydd, R. A.; Yamdagni, R. *J. Chem. Soc., Dalton Trans.* **1990**, 413.

[13] Kodama, H.; Singh, S. S. *Solid State Ionics* **1989**, *32/33*, 363.

[14] Nazar, L. F.; Liblong, S. W.; Yin, X. T. Unpublished results.

Alteration of the Substrate Specificity of 3-Oxo-Δ^5-steroid Isomerase by Mutation of the Catalytic Base (Asp-38 to Glu-38)

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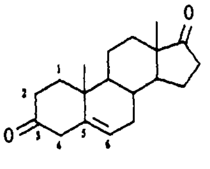
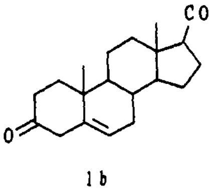
We report that mutation of Asp-38 to Glu-38 in 3-oxo-Δ^5-steroid isomerase alters the enzyme specificity, decreasing k_{cat} 300-fold toward 5-androstene-3,17-dione (**1a**) but only 32-fold toward 5-pregnene-3,20-dione (**1b**). This 10-fold difference in specificity is due to a modification of the catalytic base of the enzyme (Asp-38) rather than any change in the amino acids involved in binding.



1a



1b

3-Oxo-Δ^5-steroid isomerase (EC 5.3.3.1, also called Δ^5-3-ketosteroid isomerase, KSI) from *Pseudomonas testosteroni* catalyzes the conversion of a variety of 3-oxo-Δ^5-steroids to their conjugated Δ^4-isomers (Scheme I).[2] This reaction proceeds

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[1] (a) Department of Chemistry and Biochemistry. (b) Department of Biological Sciences. (c) Center for Advanced Research in Biotechnology.

[2] For reviews on the mechanism of 3-oxo-Δ^5-steroid isomerase, see: (a) Pollack, R. M.; Bounds, P. L.; Bevins, C. L. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 559. (b) Batzold, F. H.; Benson, A. M.; Covey, D. F.; Robinson, C. H.; Talalay, P. *Adv. Enzyme Regul.* **1976**, *14*, 243.