In the other more apolar solvents, the balance of the forces favors the opposite screw sense.

Addition of small amounts of HFP to the chloroform solution induces the progressive inversion of the helix, revealed by the decrease of the positive couplet and then by the gradual appearance of a couplet having opposite chirality (Figure 2).

At about 3% HFP concentration and 20 °C, the optical activity in the 280-nm region is practically zero, corresponding to a 50:50 composition of right-handed and left-handed helices. The temperature decrease shifts the equilibrium toward formation of the negative couplet, thus suggesting that the right-handed 3_{10}-helix is the more stable conformation at low temperature. At −11 °C the molar ellipticity was −8000 at 295 nm and +5800 at 265 nm.

3_{10}-Helices of both screw senses have been frequently found in homooligopeptides of aminoisobutyric acid, $(\mathrm{Aib})_n$, owing to the absence of chiral residues.[5,11,12] Indeed, Jung was able to reveal their interconversion in solution by freezing the equilibrium at very low temperature.[12] $(\mathrm{Aib})_n$ peptides, however, can be considered a "racemate" of the two enantiomeric helices at any conditions. The dehydropeptide described here, by contrast, was able to adopt preferentially either the left-handed or the right-handed 3_{10}-helix, the interconversion between the two enantiomeric helices depending on temperature and solvent conditions.

The result confirms the unique conformational features of dehydropeptides, which may be also of interest as models for conformational energy investigation of more complex biological structures.

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Peculiar Chirality in a Hydrothermally Synthesized One-Dimensional Molybdenum Phosphate Polymer: Structure of $(Et_4N)_2[Mo_4O_8(PO_4)_{2/2}(H_{1.5}PO_4)_2]\cdot 2H_2O$

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Compared to the more familiar organic polymers, there is a relative paucity of structural data known for one-dimensional (1-D) inorganic systems. While inorganic polymers from the lighter main-group elements, such as S, N, and P, contain covalent bonds and often have structures reminiscent of their organic counterparts, metal–metal bonds can also connect the monomers as in the 1-D Chevrel phase materials and the well-known platinum chain compounds. Oxygen and the other chalcogens often lend themselves to the formation of extended chain materials like SiS_2, SeO_2, Sb_2O_3, and HgO as well as numerous types of silicates, especially those of the pyroxene group such as Na_2SiO_3.[1] Isolated one-dimensional chains are not common for transition-metal oxides, but examples are provided by $Mo(OH)_3PO_4$[2] and $VO(HPO_4)\cdot 4H_2O$.[3] We recently reported a 1-D sodium-bridged molybdenum phosphate polymer[4] as well as a new class of microporous solids based on the octahedral–tetrahedral framework molybdenum phosphates.[5–8] Molecular, layered, and nonporous 3-D molybdenum phosphates[9] are also known. In this paper we describe $(Et_4N)_2[Mo_4O_8(PO_4)_{2/2}(H_{1.5}PO_4)_2\cdot 2H_2O]$ (**1**), a chiral, 1-D molybdenum phosphate polymer built up from Mo_4O_4 cubes and PO_4 tetrahedra.

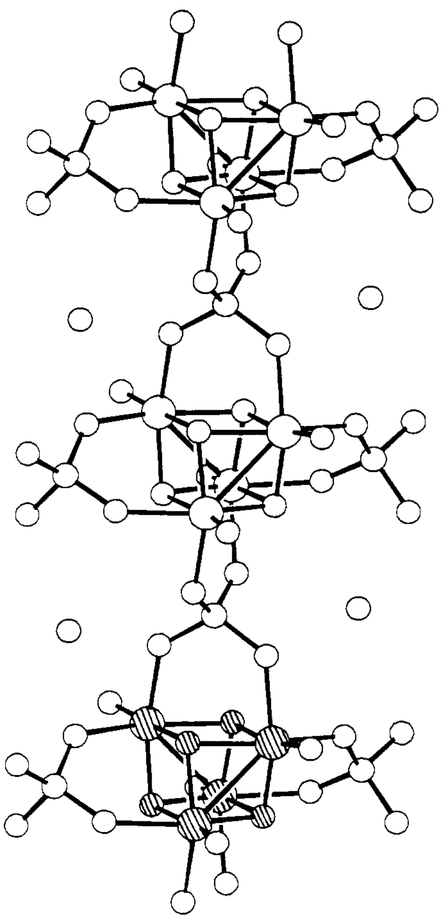

Figure 1. View of the 1-D chain which runs along [001]. The large circles represent the Mo atoms, the tetrahedrally coordinated circles the P atoms and the remaining circles the O atoms. The circles with no bonds drawn to them are the O atoms of water molecules. One of the Mo_4O_4 units has had the Mo and O atoms striped to emphasize the cubane-like geometry.

Phosphate **1**, which crystallizes as dark orange needles with a psuedohexagonal cross section, is isolated in 80% yield from the reaction of $Et_4N\cdot OH$, $Mo(<2\mu)$, MoO_3, H_3PO_4, and H_2O in a mole ratio of 15:1:5:20:250 at 200 °C for 112 h and is the only solid separating from solution. It is single phase as judged from comparison of the powder X-ray diffraction pattern to the pattern calculated from the fractional coordinates from the single-crystal study discussed below.

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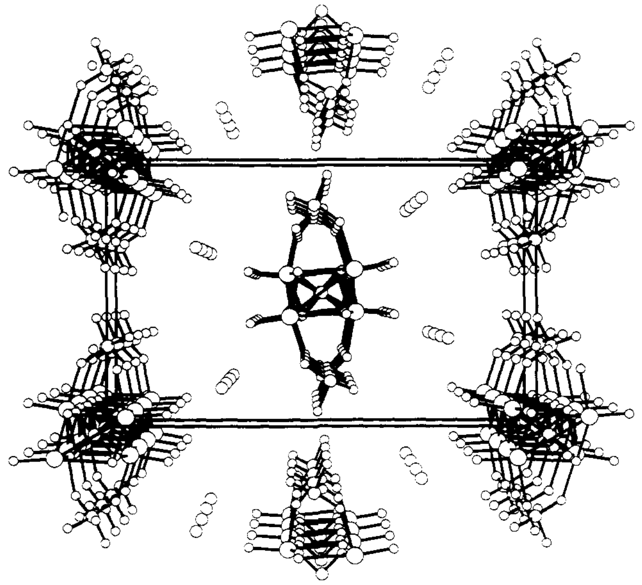

Figure 2. The unit cell of **1** viewed down [001] showing the chains hydrogen bonded into layers. Only the N atoms of the interlamellar Et_4N^+ cations are shown.

The structure of **1** was refined in the orthorhombic space group $P2_12_12$[10] and consists of 1-D chains, which run parallel to [001], of Mo_4O_8 cubane-like units and $H_{1.5}PO_4$ and PO_4 tetrahedra. Two basic types of Mo_4O_4 cubes have been observed to date, types A and B. Type A: cubes with rigorous point symmetry $\bar{4}3m$ and six equivalent Mo–Mo bonds near 2.55 Å which describe a perfect tetrahedron with all six cube faces coordinated to two O atoms of a PO_4 group as found in $Cs_3Mo_4P_3O_{16}$[11] and $(NH_4)_3Mo_4P_3O_{16}$.[7] Type B: more distorted "cubes" (Figure 1) which have approximate or rigorous point symmetry $\bar{4}2m$ resulting from the elongation of the cube in one direction perpendicular to two opposite faces. These cubes have four of the six cube faces coordinated to PO_4 groups with four Mo═O groups and two Mo–Mo bonds near 2.6 Å on the remaining two opposite cube faces. The cubes in **1** are of type B and been observed in several materials.[5,12-14]

Each cube combines with 2/2 PO_4 groups, which forms the chain of alternating cubes and PO_4 tetrahedra, as well as with two $H_{1.5}PO_4$ units (Figure 1). The protons on the terminal PO_4 groups were assigned as follows: since the Mo are 5+ (as determined from (a) the characteristic geometry of the short molybdenyl groups (ca. 1.6 Å) trans to a long Mo–O (ca. 2.3 Å), (b) the observation of a Mo–Mo single bond, and (c) bond strength-bond length calculations[15] which indicate valences of 5.0+ and 4.8+ for Mo(1) and Mo(2), respectively), charge neutrality requires 1.5 H^+ per PO_4. Since it would be very unlikely that both O(11) are protonated due to their close contact of 2.28 (5) Å, O(10) must be an OH group and the remaining H^+ is shared between the two interchain O(11) atoms. This is very similar to the geometry and short H bonds recently observed by Effenberger and co-workers (vide infra). The $H_{1.5}PO_4$ groups cap the two cube faces that are 90° from the chain direction and 90° from the molybdenyl Mo═O vectors. The chains are hydrogen bonded into 2-D sheets via unusual P–O···H··O–P groups as shown in Figure 2, which shows the unit cell contents along [001], which is parallel to the chain direction. The O(11)–O(11) interchain-hydrogen-bonded contact is extremely short at 2.28 (5) Å. While "bent" OH···O hydrogen bonds are usually around 2.7–3.0 Å and "linear" H bonds are ca. 2.4–2.6 Å,[16] H bonds in the range of the one found here (<2.4 Å) have been discovered very recently by Effenberger in several phosphate or arsenate materials.[17] The hydrogen bonds found here, closely resembling geometrically those characterized by Effenberger,[17] are shown in Figure 3. While the standard deviations found in this structure are relatively high, probably due to the somewhat fibrous nature of the crystals, which resulted in weak scattering, the *R* factors, the other observed bond lengths, bond strength–bond length calculations, and residual electron density are all very reasonable, which suggests that the very short O(11)–O(11) contact is probably one of the shorter O–O hydrogen-bonded contacts known.

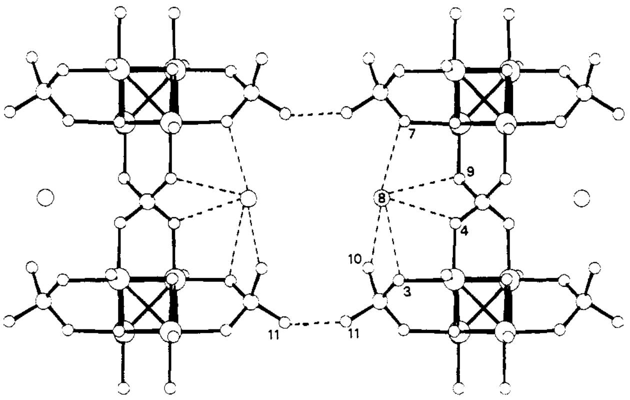

Figure 3. The interchain-hydrogen-bonded network projected onto (010). Selected bond lengths (Å): Mo–Mo, 2.637 (4); O(11)–O(11), 2.28 (5); O(10)–O(8), 2.94 (4); O(8)–O(3), 3.14 (4); O(8)–O(9), 3.11 (4); O(8)–O(4), 2.98 (4); O(8)–O(11), 3.37 (4).

This polymer displays an unusual kind of chirality that is not due to the helical packing of achiral entities like those found in quartz or $NaClO_3$. The dissymmetry is not due to one single asymmetric atom as found in carbon chemistry, nor can the tetrahedrally coordinated intrachain P atoms be considered analogous to the spiro atoms in certain chiral compounds (e.g., the tetramethylspirobipyrrolidinium cation) as this PO_4 group and its two associated cubes together are larger than the unit cell repeat distance. The chirality is inherent in each 7.5-Å repeat unit of the chain. The important point is that the individual chains, even when considered as isolated entities removed from the crystal, are chiral with point symmetry 222. All chains in an individual crystal have the same handedness. Each layer of hydrogen-bonded chains has a polar direction, but in accord with the fact that crystals of point group 222 cannot have polar axes,[18] every other layer parallel to (100) has its polar axis alternating parallel to [001] and [00$\bar{1}$]. The other enantiomer not reported here has a slightly higher *R* factor (5.2 vs 5.0%).

Preliminary attempts to solubilize the polymer chains to investigate their properties in solution have not been successful.

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Supplementary Material Available: Experimental crystallographic details for **1** including crystal data, intensity measurements, details of structure solution and refinement, and tables of positional parameters, *U* values, intramolecular distances and angles, and intermolecular distances (19 pages); listing of observed and calculated structure factors for **1** (11 pages). Ordering information is given on any current masthead page.

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(10) Crystallographic data for **1**: orthorhombic, space group $P2_12_12$ with a = 12.235 (8) Å, b = 19.141 (4) Å, c = 7.497 (4) Å, Z = 4, V = 1756 (2) $Å^3$, and R (R_w) = 0.050 (0.050). Anisotropic refinement for Mo and P with all other atoms isotropic with 702 data for 113 variables. Max (min) residual electron density = 1.24 (−0.65) $e \cdot Å^{-3}$.

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