preliminary magnetic susceptibility and EPR studies do not show the contributions that would arise from charge-localized, paramagnetic ($S = {}^1/_2$) D^+ monocations (D = ET, TMTSF). This suggests that the charge on the cation network is delocalized, with average oxidation state $D^{+2/3}$. This suggestion is consistent with the fact that the conductivity of **1** (**2**) is ca. 6 (5) orders of magnitude greater than that of the charge-localized system[12] $[PT]_3[InI_4]_2$ ($\sigma_{RT} = 2.5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$). The delocalization in **1** appears to be mediated not only by short (≤3.6 Å) S-S contacts within the ET stacks but also by numerous short (≤3.6 Å) dmit-ET and dmit-dmit S-S contacts. From the known properties[4,5] of conducting salts utilizing bis(dichalcogenide) complexes, we expect to find higher conductivities and new phenomena in materials that employ open-shell or partially oxidized tris(dichalcogenides).

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Supplementary Material Available: A table of fractional coordinates and B_{eq} values (Å^2) for the atoms of $[ET]_3[V(dmit)_3]_2$ (1 page). Ordering information is given on any current masthead page.

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[13] ET 1 (ET 2): central C═C, 1.382 (14) Å (1.352 (9) Å); central C—inner S, 1.722 (8) Å (1.734 (13) Å); outer C—inner S, 1.734 (16) Å (1.738 (16) Å). For a given entry, the number in parentheses is the standard deviation of a single observation and is the larger of that estimated from the inverse matrix or from the averaging of values assumed to belong to the same population. The differences between the two ET cations are not significant. In $[PT]_3[InI_4]_2$,[11] ESR measurements support a localized picture of different charges on the two independent PT cations.

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Synthesis of a New One-Dimensional Sodium Molybdenum Phosphate Polymer: Structure of $[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]^{2-}$

While the generation of molybdenum phosphate polyanions in solution has been known for nearly 175 years,[1] most of these compounds have the molybdenum near an oxidation state of 6+, and little is known about materials with lower oxidation states. However, in the solid state, we and others have found a new class of octahedral-tetrahedral frameworks, based on the system M-Mo-P-O (M = metal cation), which displays a great structural diversity and contains several novel layer and tunnel structures. Examples of these solids include $Cs_2Mo_4P_6O_{26}$,[2] $Cs_4Mo_8P_{12}O_{52}$,[2] $AgMo_5P_8O_{33}$,[3] $CsMoP_2O_7$,[4] $Cs_4Mo_{10}P_{18}O_{66}$,[5] $Cs_4Mo_6P_{10}O_{38}$,[6] and $Mo_3P_5SiO_{19}$[7] as well as metal-metal-bonded $Mo_4O_4^{6+}$ cubes in $Cs_3Mo_5P_6O_{25}$[8] and $Cs_3Mo_4P_3O_{16}$,[9] all of which contain Mo in an oxidation state less than 6+. Since these reduced molybdenum phosphates were so abundant in the solid state, we were interested to see if any corresponding solution species were capable of existence in addition to the metal-metal-bonded molybdenum phosphate of Bino and Cotton.[10] This paper describes the synthesis and structure of a one-dimensional polymeric sodium molybdenum phosphate, $(PPh_4)_2[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]\cdot 5H_2O$ (**1**).

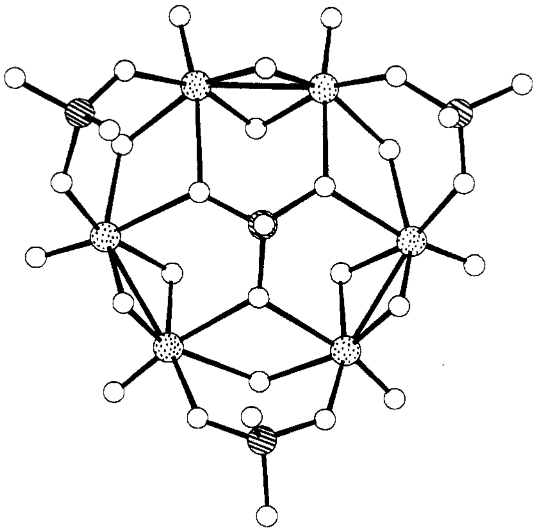

Figure 1. View down the approximate 3-fold axis in the $Mo_6P_4O_{24}(OH)_7^{5-}$ anion as drawn by Chem-X 88.[13] The bonding and nonbonding Mo-Mo contacts are 2.599 (1), 2.588 (2), 2.588 (1) Å and 3.590 (1), 3.580 (2), 3.591 (2) Å, respectively. The stippled atoms are Mo, the striped atoms P, and the remaining atoms O.

Large orange crystals of **1** were first observed in the hydrothermal reaction of Na_2MoO_4, Mo, H_3PO_4, PPh_4Br, and H_2O in a mole ratio of 2.6:1.3:8.2:1:141 at 130 °C for 24 h. Under these conditions the major product is a blue, unidentified microcrystalline material that can be easily separated from the title compound, which is obtained in ca. 30% yield, by trituration and dispersion of the blue solid into water. The presence of a reducing agent, in this case Mo metal, is necessary to reduce the Mo^{6+} starting materials and avoid the formation of the familiar Keggin type heteropolymolybdates.

Solution of the single-crystal X-ray data[11] shows the formula of the orange crystals to be $(PPh_4)_2[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]\cdot 5H_2O$. The main structural unit in **1** is a $Mo_6P_4O_{24}(OH)_7^{5-}$ cluster (Figure 1), which has no crystallographically imposed symmetry but has an approximate 3-fold axis. The six Mo atoms, which each have a terminal molybdenyl group, lie in a plane (maximum deviation 0:04 Å), are connected by 12 bridging O atoms, and display alternating bonding and nonbonding Mo-Mo contacts. There are four phosphate groups in **1**. Three of these phosphate groups are on the periphery of the cluster and have two terminal OH groups, while the unique central phosphate has three oxygen atoms that span the nonbonding Mo-Mo contacts and one terminal OH group. On the basis of bond-strength-bond-length calculations, the presence of a Mo-Mo single bond, and the ob-

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[1] Leppert, D. L. Isopolyanions and Heteropolyanions. In *Comprehensive Inorganic Chemistry*; Pergamon Press: Oxford, England, 1973; Vol. 4, Chapter 51, pp 607-672. Greenwood, N. N. In *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984; p 1184.

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[3] Lii, K. H.; Johnston, D. C.; Goshorn, D. P.; Haushalter, R. C. *J. Solid State Chem.* **1987**, *71*, 131.

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[9] Haushalter, R. C. *J. Chem. Soc., Chem. Commun.* **1987**, 374.

[10] Bino, A.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 462.

[11] Crystal data for **1**: triclinic, space group $P\bar{1}$ (No. 2), −115 °C, a = 17.314 (9) Å, b = 18.181 (7) Å, c = 13.232 (2) Å, α = 110.50 (2)°, β = 93.29 (3)°, γ = 63.42 (3)°, V = 3465 (2) Å^3, Z = 2, d_{calc} = 1.962 g cm^{-3}. For Mo Kα, μ = 12.7 cm^{-1} and an empirical absorption correction was applied. Use of direct methods on 8458 data with $2\theta_{max}$ = 50° and $I > 3\sigma(I)$ gave R (R_w) = 0.041 (0.046) for 896 variables. Maximum and minimum values of the residual electron density were <±1.44 e Å^{-3}. Positional parameters and isotropic temperature factors are given in Table I (supplementary material).

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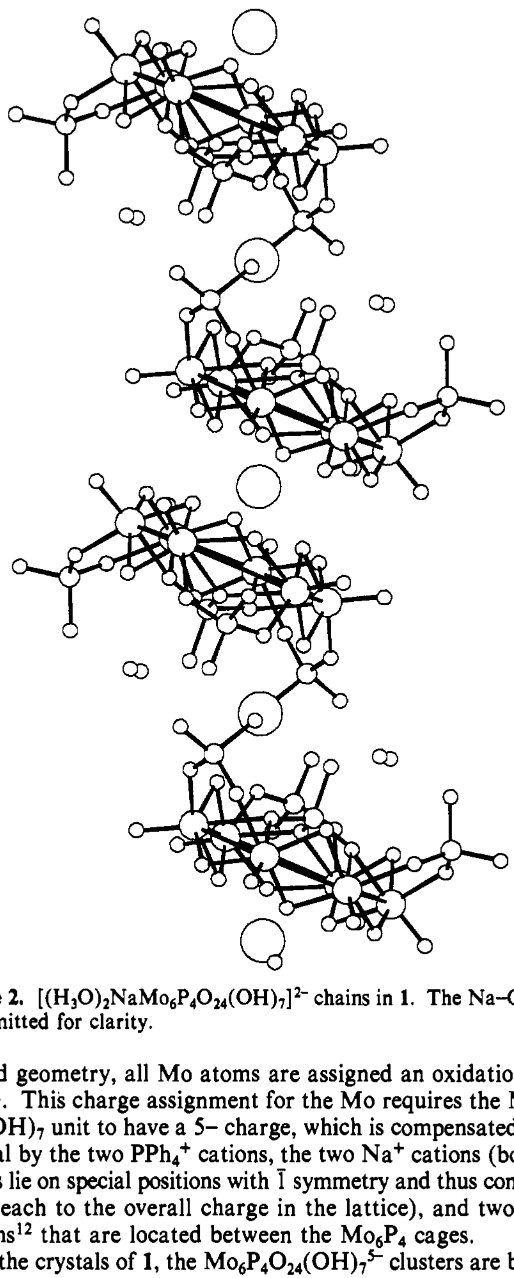

Figure 2. $[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]^{2-}$ chains in **1**. The Na-O bonds are omitted for clarity.

served geometry, all Mo atoms are assigned an oxidation state of 5+. This charge assignment for the Mo requires the $Mo_6P_4O_{24}(OH)_7$ unit to have a 5- charge, which is compensated in the crystal by the two PPh_4^+ cations, the two Na^+ cations (both Na atoms lie on special positions with $\bar{1}$ symmetry and thus contribute $+^1/_2$ each to the overall charge in the lattice), and two H_3O^+ cations[12] that are located between the Mo_6P_4 cages.

In the crystals of **1**, the $Mo_6P_4O_{24}(OH)_7^{5-}$ clusters are bridged together into one-dimensional strings (Figure 2), which run parallel to the [001] direction, by two sodium ions, Na1 and Na2, both of which lie on inversion centers and are coordinated to oxygens in a distorted-octahedral fashion. The Na1 ion is coordinated to six μ_2-O atoms, while Na2 is bound to two μ_2-O and four phosphate OH oxygens. There are also two hydronium cations sandwiched between every other $Mo_6P_4O_{24}(OH)_7^{5-}$ cluster[12] (Figure 2). These $[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]^{2-}$ clusters are hydrogen-bonded into two-dimensional sheets, which lie parallel to the *ac* face of the unit cell, by five additional water molecules per formula unit. These sheets are interleaved with layers of the PPh_4^+ cations to complete the three-dimensional structure.

These results, together with our recently determined structure of the huge $[Na_{12}Mo_{24}P_{17}O_{97}(OH)_{31}]^{8-}$ cluster,[6] demonstrate that it is possible to form novel metal-metal-bonded molybdenum phosphate clusters from aqueous phosphoric acid in the presence of a suitable reducing agent. Preliminary experiments indicate that reactions similar to those discussed here with sulfuric acid in place of phosphoric acid likewise yield reduced molybdates.

Supplementary Material Available: Tables of crystallographic parameters, positional and thermal parameters, and bond lengths and bond angles (19 pages); a table of observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

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[12] Since all of the Mo atoms are assigned an oxidation state of 5+, as discussed in the text, the presence of two hydronium cations is required for charge balance. It was not possible to crystallographically locate the hydrogen atoms on any of the water/hydronium molecules in the structure, but it is assumed that the oxygen atoms between the $Mo_6P_4O_{24}(OH)_7^{5-}$ clusters are hydronium cations due to their proximity to the negative charges on the cluster.

[13] Chem-X is designed and distributed by Chemical Design, Ltd., Mahwah, NJ.

Regioselectivity in the Novel Conversion of an Aromatic C-F Bond into a C-H Bond via an Organonickel Intermediate

During an attempt to synthesize the phosphonium cation $[Ph_3(C_6F_5)P]^+$ by a procedure analogous to that reported in the literature for $[Ph_4P]^+$, we have discovered an unusual and unexpected C-F cleavage reaction. This cleavage reaction involves the formation of an organometallic intermediate whereby a C-Ni bond has replaced a C-F bond in the 4-position of the perfluoro ring. Subsequent hydrolytic cleavage of the C-Ni bond results in C-H bond formation.

The compound $[Ph_4P]Br$ has been previously prepared by the fusion reaction between triphenylphosphine, bromobenzene, and nickel bromide (eq 1).[1] Subsequent hydrolysis of the tetraphenylphosphonium nickelate salt gives the bromide salt $[Ph_4P]Br$.

$$\mathrm{2PPh_3 + PhBr + NiBr_2 \rightarrow [Ph_4P][NiBr_3(PPh_3)]} \qquad (1)$$

Our approach to the synthesis of the compound $[Ph_3(C_6F_5)P]Br$ is to carry out an analogous fusion reaction with triphenylphosphine, bromopentafluorobenzene, and nickel bromide. We find that the reaction mixture must be refluxed in an open vessel under a nitrogen flow because heating the mixture in a sealed tube gives triphenylphosphine oxide as the product after hydrolysis. Treating the fusion product from the open-vessel reaction with water results in the formation of the compound $[Ph_3(4\text{-}C_6F_4H)P]Br$ (eq 2), whereby the fluorine in the 4-position has been replaced by hydrogen.[2]

$$\begin{aligned}&\mathrm{PPh_3 + C_6F_5Br + NiBr_2 \xrightarrow[N_2]{\sim 200\ ^\circ C} solid}\\&\mathrm{solid + H_2O \rightarrow [Ph_3(4\text{-}C_6F_4H)P]Br}\end{aligned} \qquad (2)$$

This hygroscopic salt $[Ph_3(4\text{-}C_6F_4H)P]Br$ dissolves in water, and this solution gives a precipitate of silver bromide with aqueous silver nitrate solution. The $^{31}P\{^1H\}$ NMR spectrum of the salt shows a triplet centered at δ 16.2 (^3J(PF) = 6.0 Hz). The ^1H NMR spectrum shows a complex multiplet in the phenyl region, and no individual C-H resonance on the fluoro aromatic ring can be identified. The ^{19}F NMR spectrum shows two multiplets of equal intensity centered at δ -123.5 (F^a) and δ -131.3 (F^b). Proton decoupling results in the simplification of each set of fluorine multiplets. Hydrolysis of the fusion product with D_2O rather than H_2O yields the deuterated derivative $[Ph_3(4\text{-}C_6F_4D)P]Br$. The ^2H NMR spectrum of this salt shows a broad multiplet in the phenyl region at δ 7.81, and the IR spectrum shows a band at 2196 cm^{-1} characteristic of ν(C-D). Final confirmation of the structure of these phosphonium salts is by spectral simulation of the ^{19}F NMR spectrum of $[Ph_3(4\text{-}C_6F_4H)P]Br$. Iterative fitting to the experimental spectra

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[1] Horner, L.; Mummenthey, G.; Moser, H.; Beck, P. *Chem. Ber.* **1966**, *99*, 2782-2788.

[2] Heating triphenylphosphine (3 g, 1 mol) with bromopentafluorobenzene (5.65 g, 2 mol) and nickel bromide (1.25 g, 0.5 mol) under nitrogen at reflux in an oil bath at 200 °C for 3 h gave an uncharacterized fused product. Subsequent hydrolysis resulted in the isolation of $[Ph_3(4\text{-}C_6F_4H)P]Br$ (1 g). Anal. Calcd for $C_{24}H_{16}BrF_4P$: C, 58.7; H, 3.28. Found: C, 58.8; H, 3.45.

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