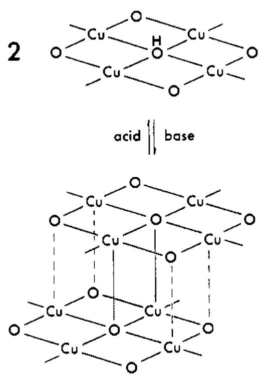
Scheme I



moiety is a five-coordinate oxo anion (Ox), which is displaced by 0.29 Å from the mean plane of the four copper ions. The coordination sphere of Ox is completed by Cu(2′), a copper atom from a second macrocyclic unit. This bond and the symmetry-related Cu(2)–Ox′ linkage hold the two macrocyclic units together in a centrosymmetric dimer. In addition, there are weaker interactions involving Cu(1) and Cu(3).

The outer faces of the dimer are blocked by perchlorate ions, which are bound, in tripod fashion, to the Cu_4 array. Perchlorate oxygen atoms O(11) and O(12) are each coordinated to a single copper atom (O(11)–Cu(4) = 2.519 (8) Å, O(12)–Cu(3) = 2.624 (8) Å), and the interatomic distances, while rather long, are within the range observed for axial copper–oxygen bonds.[5] Atom O(14) has somewhat longer interactions with both Cu(1) and Cu(2). The inequivalence of these interactions is not surprising in view of the geometric mismatch between the square-planar Cu_4 array and the tetrahedral perchlorate anion. It is significant, however, that the shortest $Cu{-}OClO_3$ distance involves Cu(4), which has no significant axial interaction on the opposite side of the macrocycle, while the longest $Cu{-}OClO_3$ distance is that to Cu(2), which has a strong axial bond to Ox′. These observations support the suggestion that distinct bonding interactions are present, rather than more generalized electrostatic interactions or crystallographic packing effects. To our knowledge, this is the first structurally characterized example of perchlorate binding as a tripod ligand, although a number of bridging perchlorate ions involving one[6] or two[7] oxygen atoms have been reported. Neither the second perchlorate anion nor the solvate water molecule exhibits any significant intermolecular contacts.

The electronic reflectance spectrum of solid **2** (λ_{max} = 620 nm) corresponds closely to the solution spectrum (λ_{max} = 621 nm in dmf), suggesting that the octacopper structure is maintained in solution. The reflectance spectrum of the unrecrystallized material **3** (λ_{max} = 648 nm) is also similar to that of a fresh dmf solution (λ_{max} = 647 nm); however, the solution spectrum changes slowly with time and, after approximately 3 days, is identical with that of **2**. The same spectral change is accomplished within a few seconds in the presence of a noncoordinating base such as triethylamine. Addition of small amounts of acid will reverse the reaction, but excess acid leads to other, as yet unidentified, products. Very similar behavior is observed for the tetracopper complex **1** (λ_{max}(solid) = 670 nm, λ_{max}(in dmf) = 672 nm fresh, changing to 627 nm). Recrystallization of **1** from dmf yields an octacopper complex[8] with a structure very similar to that of **2**. These results will be discussed in detail in a subsequent paper.

The spectroscopic data imply that both **1** and **3** undergo slow dimerization in dmf to yield octacopper complexes and that the reaction is promoted by base and reversed by acid. This behavior can be ascribed to competition for the central atom (Ox) between protons and macrocycle-bound copper atoms (Scheme I). In protic solutions such as ethanol the tetracopper monomer with hydroxide at the center is favored. In less protic dmf solution the octacopper species is preferred but the rate of the interconversion is slow; addition of base increases the rate by promoting dissociation of the hydroxo proton. It might be expected that the dimerization would be reversed in protic solvents; however, due to the very low solubility of **2** in these solvents, we have been unable to test this hypothesis. The core of the octacopper complex (Scheme I) resembles a fragment of a metal oxide structure with Cu–Cu distances of approximately 2.9 Å; it might therefore be expected to show some adsorptive or catalytic properties. This suggests the interesting possibility of carrying out metal-promoted reactions on the open faces of the dimer. Investigations on the binding of substrates other than perchlorate are in progress. Interactions between the metal centers are also of interest; preliminary magnetic studies indicate strong antiferromagnetic coupling within the complex. The total magnetic moment for the system falls from 2.303 μ_B at 300 K to 0.149 μ_B at 6 K; the corresponding figures for the tetranuclear complex **1** are 2.512 and 0.737 μ_B. The slight increase in antiferromagnetic coupling in the octacopper complex may indicate some exchange between the two macrocycles, via the Cu(2)–Ox′ and Cu(2′)–Ox bridges. A detailed study and theoretical analysis of the magnetic results is under way.[9]

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates, a fully labeled diagram, and crystallographic details for **2** and electronic spectra (8 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Conductive Molecular Crystals from Three-Dimensional Building Blocks: Synthesis and Characterization of Tris(bis(ethylenedithio)tetrathiafulvalenium) Bis(tris(2-thioxo-1,3-dithiole-4,5-dithiolato)vanadate), $[ET]_3[V(dmit)_3]_2$, and the Corresponding Tetramethyltetraselenafulvalenium Salt

In recent years planar transition-metal bis(dithiolene) and bis(diselenolene) complexes have received attention as building blocks for the design of highly conducting molecular solids[1-5]

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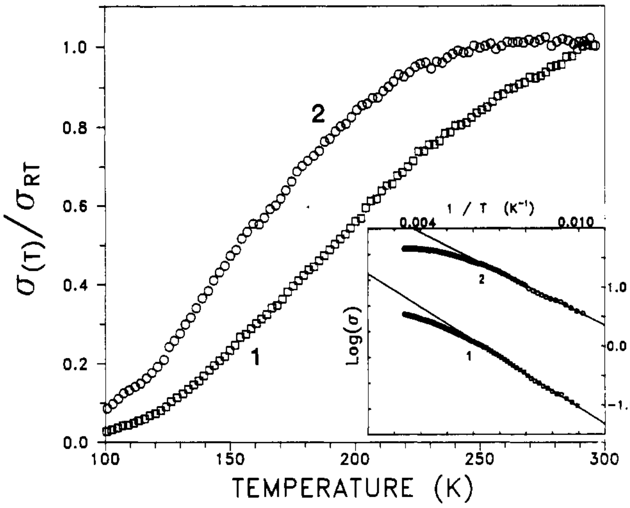

Figure 1. Four-probe, single-crystal conductivities of $[ET]_3[V(dmit)_3]_2$ (**1**) (squares) and $[TMTSF]_3[V(dmit)_3]_2$ (**2**) (circles) taken along their needle axes as a function of temperature. Conductivity values are normalized to room temperature values (see text). Inset: Plot of log σ vs $1/T$ showing the activated behavior of **1** and **2**.

(molecular metals). These complexes are attractive components for molecular metals because of their highly delocalized electronic structure, their range of stable oxidation states, and their propensity to adopt linear chain structures in the solid state.[1,6] Close intermolecular contacts of the chalcogen atoms of these complexes can produce conductive crystals that exhibit quasi-two- or three-dimensional character, as is found in the organic superconductors.[7] In particular, Ni, Pd, and Pt complexes of the dmit[8] ligand exhibit high electrical conductivities, and one of these, $[TTF][Ni(dmit)_2]_2$, exhibits a superconducting transition at 1.62 K and 7-kbar hydrostatic pressure.[4]

The use of *three*-dimensional building blocks offers new prospects for the synthesis of molecular conductors. Group V, VI, and VII transition-metal tris(dichalcogenide) complexes, which generally exhibit trigonal-prismatic coordination geometry about the metal for neutral and monoanionic complexes,[6] can undergo strong intermolecular interactions both along and perpendicular to the trigonal axis and thus are intrinsically shaped to form multidimensional networks. The work reported here demonstrates that they form the basis for a new class of molecular conductors. We present the synthesis and preliminary physical characterization of the first molecular conductors that utilize a tris(dithiolene) complex, namely the $[V(dmit)_3]$ anion.

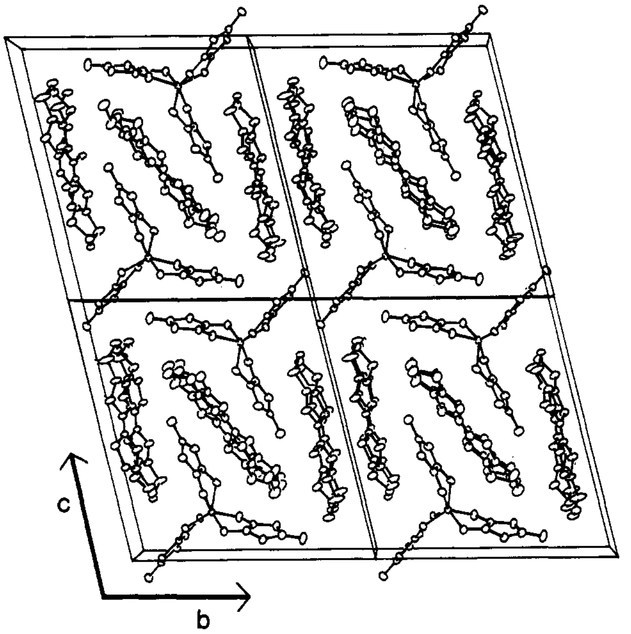

Figure 2. Molecular packing diagram of $[ET]_3[V(dmit)_3]_2$ (**1**). The view is down the *a* (needle) axis. The ellipsoids are drawn at their 50% probabilities. Hydrogen atoms have been omitted.

Tetraalkylammonium salts of $[V(dmit)_3]^-$ were prepared as described elsewhere.[9] Lustrous, dark-purple needles of $[D]_3[V(dmit)_3]_2$, (D = ET (**1**); D = TMTSF (**2**))[10] were crystallized at a platinum-wire electrode by constant-current (2 μA) electrolysis of a 1,1,2-trichloroethane solution of $[N(C_4H_9)_4][V(dmit)_3]$ (0.5 mM) and the appropriate heterofulvalene (1 mM).

Four-probe ac (27 Hz) conductivity measurements show that **1** and **2** display high conductivity along their needle axes with σ_{RT} ca. 3 and 45 Ω^{-1} cm^{-1}, respectively. The temperature dependence of the conductivity of **1** is semiconducting over the entire temperature range studied, with a well-defined activation energy of $E_a = 0.025$ eV for $T <$ ca. 170 K (Figure 1). The conductivity of **2** displays weakly metallic behavior near room temperature and a broad plateau, and then decreases, with a well-defined activation energy ($E_a = 0.020$ eV) below ca. 150 K.

The structure of **1** has been determined by single-crystal X-ray crystallography,[11] and a packing diagram of the structure is shown in Figure 2. The unit cell contains one independent $[V(dmit)_3]$ anion and two independent ET cations (cation and anion refer to positive and negative species, respectively, not necessarily possessing integer charges), one of which has a crystallographically imposed center of symmetry. The coordination about the V center is that of a trigonal prism. The $[V(dmit)_3]$ anions form an interlocking herringbone network along the *b* direction that results from face-to-face overlap of two of the dmit ligands. The remaining dmit ligand of each $[V(dmit)_3]$ anion interdigitates the ET cations. The ET cations stack side-on along the needle (*a*) axis.

The possibility that the two independent ET cations possess different oxidation states[7] is raised by such an interpretation for the PT cations in the related semiconducting compound $[PT]_3[InI_4]_2$.[12] Consideration of the inner C=C and C—S bond lengths within the ET units of **1** does not support this possibility.[13] Indeed,

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(8) Abbreviations used: $dmit^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolato; TTF = tetrathiafulvalenium; ET (or BEDT-TTF) = bis(ethylenedithio)tetrathiafulvalenium; TMTSF = tetramethyltetraselenafulvalenium; PT (or BPDT-TTF) = bis(1,3-propanediyldithio)tetrathiafulvalenium.

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(10) Anal. Calcd for **2**, $C_{48}H_{36}S_{30}Se_{12}V_2$: C, 21.97; H, 1.38; S, 36.65. Found: C, 22.01; H, 1.45; S, 36.39. The stoichiometry of **1** was confirmed by X-ray crystallography (vide supra).

(11) Crystal data for **1**, $C_{48}H_{24}S_{54}V_2$: triclinic, C_i^1-$P\bar{1}$, $a = 6.390$ (2) Å, $b = 17.536$ (6) Å, $c = 19.167$ (7) Å, $\alpha = 103.37$ (3)°, $\beta = 85.86$ (2)°, $\gamma = 90.28$ (1)°, $Z = 1$, $T = 223$ K. FACS-I diffractometer, Mo Kα radiation, $R(F^2) = 0.120$ for 9115 absorption-corrected observations, 469 variables, $R(F) = 0.057$ for 4264 observations with $F_o^2 > 3\sigma(F_o^2)$.

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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**).

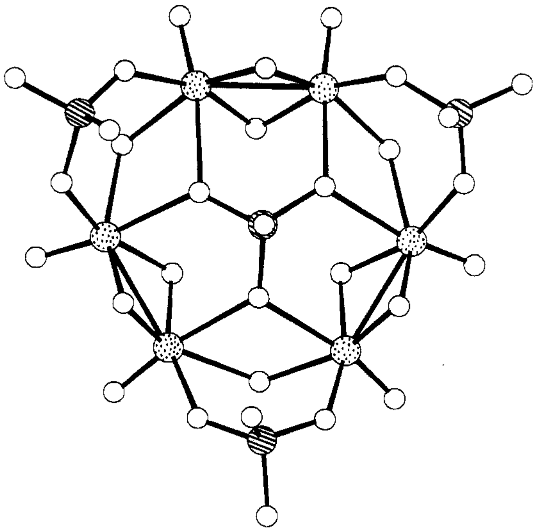

Figure 1. View down the approximate 3-fold axis in the $Mo_6P_4O_{24}(OH)_7^{5-}$ anion as drawn by Chem-X 88.[13] The bonding and nonbonding Mo–Mo contacts are 2.599 (1), 2.588 (2), 2.588 (1) Å and 3.590 (1), 3.580 (2), 3.591 (2) Å, respectively. The stippled atoms are Mo, the striped atoms P, and the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