°C) in 46% yield.[5] The analogous gallium compound $[Me_2Ga(\mu\text{-Sb-}t\text{-Bu}_2)]_3$ (**2**) has been prepared in 74% yield by a virtually identical procedure.[5]

X-ray analysis[6] revealed that **1** and **2** are both trimeric in the solid state. The six-membered rings of both compounds adopt a distorted twist-boat conformation that is devoid of symmetry. The structure of **1** is illustrated in Figure 1. Atoms In(1), Sb(2), Sb(3), and In(3) of **1** are approximately planar, and In(2) and Sb(1) lie 0.494 and 1.243 Å out of the idealized plane respectively. As expected, there is a significant variation in the endocyclic bond angles, particularly at antimony. The average endocyclic bond angles at In and Sb are 106.94 (5)° and 121.64 (6)°, respectively, in **1**. The In–Sb bond lengths in **1** vary from 2.822 (1) to 2.889 (1) Å. The average In–Sb bond length of 2.855 (2) Å compares with that of 2.844 (1) Å in $[(t\text{-Bu}_2Sb)(Cl)In(\mu\text{-Sb-}t\text{-Bu}_2)]_2$, the only other structurally authenticated organometallic indium stibinide.[4] Both values are close to the sum of covalent radii for In and Sb (2.84 Å) and somewhat larger than the bond distance in InSb (2.805 Å).

Films of InSb have been grown on Si(100) wafers from precursor **1** in a horizontal hot-wall reactor.[7] The temperatures of the saturator and deposition zones were 125 and 450 °C respectively, and H_2 (10 Torr) was employed as the carrier gas. Growth rates were ~1.0 μm/h. The films were characterized by X-ray photoelectron spectroscopy after etching with ionized argon. The corrected In(4d) and Sb(4d) signals at 18.5 and 33.5 eV, respectively, compare well with the literature values of 19.0 and 34–35 eV.[8] Moreover, the XPS experiments established an In:Sb stoichiometry of 1:1 and indicated that the carbon impurity level was barely above the limit of detectability by this technique (~1000 ppm). Examination of the films by X-ray diffraction indicated that they are polycrystalline. Preliminary experiments indicate that **2** is a useful precursor for the formation of GaSb.

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Registry No. **1**, 126847-96-9; **2**, 126847-97-0; $t\text{-Bu}_2SbSiMe_3$, 82363-94-8; Me_2InCl, 14629-99-3; InSb, 1312-41-0.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters (7 pages); listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(5) ^1H NMR (300 MHz, C_6D_6 TMS ext): **1**, δ 0.28 (s, 18 H, Me), 1.52 (s, 54 H, *t*-Bu); **2**, 0.41 (s, 18 H, Me), 1.52 (s, 54 H, *t*-Bu). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, TMS ext): **1**, δ 34.77 (s, $C(CH_3)_3$), 35.12 (s, $C(CH_3)_3$); **2**, 0.36 (s, $Ga(CH_3)_2$), 32.56 (s, $C(CH_3)_3$), 34.68 (s, $C(CH_3)_3$). The $In(CH_3)_2$ resonance for **1** was not observed. Satisfactory C and H analyses were obtained for **1** and **2**.

(6) Crystal data for **1**: $C_{30}H_{72}In_3Sb_3$, monoclinic, $P2_1/c$ (No. 14), a = 9.633 (3), b = 22.284 (6), c = 20.690(6) Å, β = 91.75°, V = 4439.3 Å^3, Z = 4, D(calcd) = 1.710 g cm^{-3}, $\mu(\text{Mo K}\alpha)$ = 33.4 cm^{-1}. A total of 7791 unique reflections were collected over the range $3.0 \leq 2\theta \leq 50.0°$ by using the $\theta/2\theta$ scan mode. Of these, 4929 were considered to be observed $[I > 3\sigma(I)]$. Crystal data for **2**: $C_{30}H_{72}Ga_3Sb_3$, monoclinic, $P2_1/c$ (No. 14), a = 9.392 (2), b = 22.080 (8), c = 20.453 (6) Å, β = 90.96 (2), V = 4240.9 Å^3, Z = 4, D(calcd) = 1.578 g cm^{-3}, $\mu(\text{Mo K}\alpha)$ = 37.9 cm^{-1}. A total of 7672 unique reflections were collected over the range $3.0 < 2\theta < 50.0°$ by using the $\theta/2\theta$ scan mode. Of these, 4904 were considered to be observed $[I > 3\sigma(I)]$. Both data sets were collected on an Enraf-Nonius CAD-4 diffractometer at 296 K, and corrections were made for Lorentz, polarization, and decay. The structure of **2** was solved by direct methods and that of **1** from the positional parameters for **2**. Both structures were refined by full-matrix least-squares methods. The final residuals were R = 0.053 and 0.044, and R_w = 0.060 and 0.052 for **1** and **2**, respectively.

(7) The reactor design is similar to that described by: Gladfelter, W. L.; Boyd, D. C.; Jensen, K. F. *Chem. Mater.* **1989**, *1*, 339.

(8) XPS data were obtained on a VG Scientific Escalab Mark I instrument with a Mg Kα X-ray anode. The observed binding energies were corrected for electrostatic charging by referencing to the adventitious C(1s) peak. Literature values were taken from: *The Handbook of X-ray Photoelectron Spectroscopy*; Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., Muilenberg, G. E., Eds.; Perkin-Elmer: Physical Electronics Division, 1976.

Conductive Polymer/Oxide Bronze Nanocomposites. Intercalated Polythiophene in V_2O_5 Xerogels

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During the last decade sol–gel-derived materials have attracted increasing attention from the chemical, materials science, and physics communities due to their demonstrated as well as potential value for the development of advanced structural[1] and electronic ceramics.[2] Vanadium oxide xerogels in particular are unique among sol–gel-derived materials[3] because they posses a porous layered structure with an interlayer distance of 11.55 Å[4] and they are capable of host–guest intercalation chemistry with a variety of species (i.e., alkali-metal ions,[5] alkylamines,[6] alcohols,[6] sulfoxides,[6] tetrathiafulvalene[7] (TTF), benzidine,[7] etc). The driving force for this intercalation chemistry depends on the guest species and can involve cation exchange, acid–base, or redox chemistry. $V_2O_5 \cdot nH_2O$ xerogels (n ~ 1.6–2.0) are strongly oxidizing and amenable to redox intercalation chemistry. It is well-known that organic molecules such as aniline, pyrrole and thiophene yield, upon chemical or electrochemical oxidation, technologically

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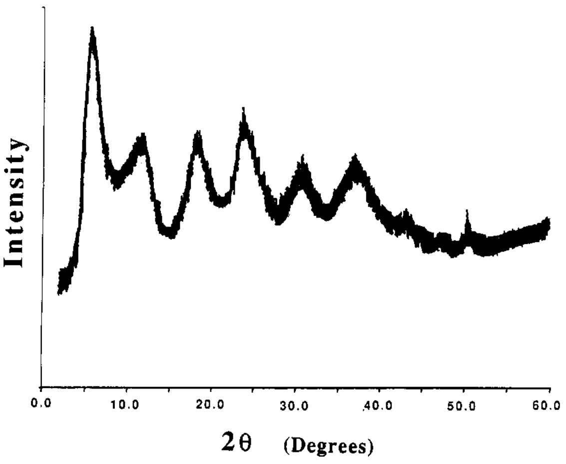
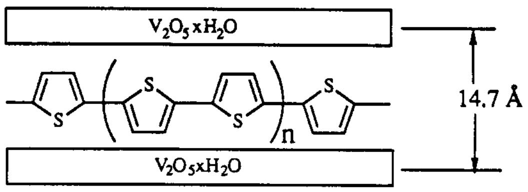


Figure 1. Typical X-ray diffraction diagram taken from films of $(C_8H_4S_2)_{0.44}V_2O_5{\cdot}0.54H_2O$.

Scheme I



promising, robust, electrically conductive polymers.[8,9] Progress in elucidating the structure of these materials is hampered by their invariably amorphous nature. The lack of structural data inhibits to a certain degree the development of accurate theoretical models aimed at understanding charge transport in these materials.[10] Furthermore, owing to their limited processability, oriented specimens for important anisotropic studies are rare or lacking. Intercalation of these conducting polymers in layered materials may be a viable approach to obtaining oriented, structurally better defined polymers with a minimal degree of cross-linking and thus improved charge-transport properties. Furthermore, such laminated conducting polymer/layered inorganic materials are interesting because they feature alternating monolayers of electrically active but chemically diverse components with potentially novel properties. This class of materials can be viewed as *polymer bronzes* by analogy to alkali-metal[11] or molecular[6] bronzes. It has been implied that in molecular-scale organic/inorganic composites, the otherwise independent band structures of each component can interact/overlap, thus giving rise to a new set of properties not possible from either component separately.[12] It has been shown that pyrrole and 2,2′-bithiophene intercalatively polymerize in FeOCl[13] to yield conductive polymer intercalation compounds in microcrystalline form. Three-dimensional matrices such as zeolites have been used to encapsulate polyaniline and polypyrrole.[14] Recently we reported the polymerization of aniline in $V_2O_5{\cdot}nH_2O$ xerogels.[15] Here we report the successful in situ intercalation/polymerization of 2,2′-bithiophene in layered $V_2O_5{\cdot}nH_2O$ xerogels to yield films of a conducting polymer/layered oxide bronze with good electrical p-type conductivity.

The reaction of 30 mL of 0.04 mM acetonitrile solution of 2,2′-bithiophene with films of $V_2O_5{\cdot}nH_2O$[4] (approximate thickness 25–35 μm) was carried out at reflux temperature for 24 h. Color change from dark red to black occurs followed by the appearance of metallic luster. The resulting product analyzes for $(C_8H_4S_2)_{0.44}V_2O_5{\cdot}0.54H_2O$[16] (I). This is a redox reaction in which the 2,2′-bithiophene monomer is oxidatively polymerized and the V_2O_5 layers are reduced, generating V^{4+} centers. Thiophene itself, which is more difficult to oxidize, does not react with the $V_2O_5{\cdot}nH_2O$ xerogel. X-ray diffraction data (see Figure 1) reveal that $(C_8H_4S_2)_{0.44}V_2O_5{\cdot}0.54H_2O$ is layered with an interlaying spacing of 14.70 Å. The observed 3.15-Å new layer expansion represents the removal of a water layer from the intralamellar space followed by the insertion of a monolayer of polythiophene. Therefore the actual gallery height is 5.95 Å. The remaining H_2O in I is probably co-intercalated with polythiophene in the V_2O_5 intralamellar space, being either hydrogen bonded to layer oxygen atoms or coordinated to $V^{5+/4+}$ centers. Thermal gravimetric analysis (TGA) experiments under flowing oxygen show that after an initial loss of water, a thermally resistant component exists with no appreciable volatility up to 230 °C. As in the pristine xerogel no (*hkl*) or (*hk0*) reflections are observed in I, confirming the turbostratic nature of the V_2O_5 slabs perpendicular to the stacking axis.[4] Although the exact thickness of the $V_2O_5{\cdot}nH_2O$ layers is not known, the contribution of the guest species to the interlayer distance in I is estimated at ~5.95 Å, not too different from that found in $(\text{polyaniline})_{0.44}V_2O_5{\cdot}nH_2O$[15] and $(\text{polypyrrole})_{0.23}\text{FeOCl}$.[13] The polymers in these materials were proposed to be oriented with their aromatic rings perpendicular to the layers according to the model shown in Scheme I.

Infrared spectroscopy of I clearly shows the presence of polythiophene with no evidence of free 2,2′-bithiophene (the characteristic intense peaks at 823 and 809 cm^{-1} are absent). The intercalated polythiophene can indeed be isolated from I by dissolving the V_2O_5 skeleton in either 1 M HCl or 2% NaOH solutions and identified by its infrared spectrum.[10c,17]

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[16] Anal. Calcd for $(C_8H_4S_2)_{0.44}V_2O_5{\cdot}0.54H_2O$ (Galbraith Laboratories, Knoxville, TN): C, 16.01; H, 1.07; S, 10.67; V, 38.65. Found: C, 14.98; H, 1.25; S, 8.12; V, 36.48. Percent V_2O_5 by TGA (in oxygen): Calcd: 68.97; Found: 69.10.

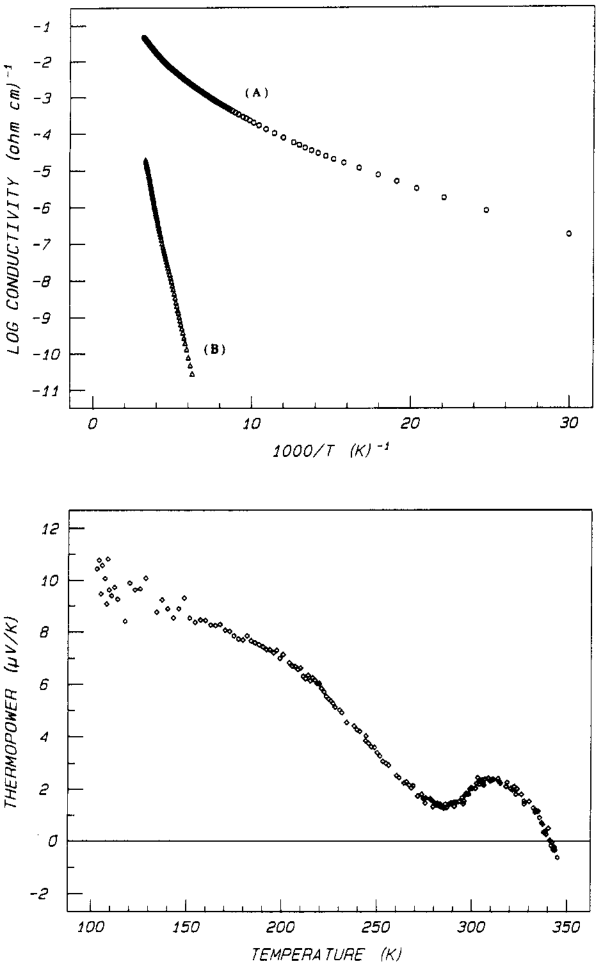

Figure 2. Top. curve (A): Four-probe variable-temperature electrical conductivity data of free-standing films of $(C_8H_4S_2)_{0.44}V_2O_5{\cdot}0.54H_2O$ (I). Curve (B): pristine $V_2O_5{\cdot}1.6H_2O$ xerogel. Bottom. Variable-temperature thermoelectric power data for $(C_8H_4S_2)_{0.44}V_2O_5{\cdot}0.54H_2O$.

Electron paramagnetic resonance, EPR, spectra (recorded at 273 and 77 K) of I show a broad signal observed at $g \sim 1.963$, which arises from interacting V^{4+} centers. The typical signal observed from polythiophene is absent suggesting the presence of antiferromagnetic exchange between the unpaired density on the polymer backbone and that in V_2O_5. The EPR signal of polythiophene[18] is observed only after the polymer is separated by dissolving the host matrix. These data show that in I phase separation to a polymer and a V_2O_5 phase does not occur. The EPR signal observed for I resembles that of $Na_{0.32}V_2O_5{\cdot}nH_2O$[19] and supports the proposed reduction of the V_2O_5 network in I.

As expected, free standing films of I show a dramatic increase in electrical conductivity by 4 orders of magnitude with respect to pristine xerogel with a room temperature value of $\sim 0.1\ \Omega^{-1}\ cm^{-1}$. Variable-temperature measurements (from 5 to 300 K) show a corresponding decrease in conductivity with falling temperature, characteristic of thermally activated behavior, similar to that observed for the bulk polythiophene polymer[20] (Figure 2). At room temperature the conductivity perpendicular to the films is at least 10 times lower than that parallel to them, indicating their anisotropic nature. Variable temperature thermoelectric power (TP) measurements show unusual behavior. At 350 K the Seebeck coefficient, S, is relatively small, $\sim -1\ \mu V/K$, and negative but quickly becomes positive (with a minimum at ~280 K) as the temperature falls and remains small and positive ($<10\ \mu V/K$) down to 100 K, the lowest temperature studied. The TP data suggest that at room temperature I is a p-type conductor with the predominant charge carriers being holes. The switch in conductivity above 340 K may suggest a change in the charge-transport mechanism with the majority carriers being electrons and the vanadium oxide layers assuming a more active role in the charge transport. The curious nonlinear temperature dependence of the TP, the carrier sign reversal, and the presence of the minimum at ~280 K currently are not understood. Thus far this phenomenon is unique to I and has not been observed previously in conductive polymer systems[21,22] or V_2O_5 xerogels.[19,22] It may be due to possible electronic interactions between the polythiophene polymer chains and the V_2O_5 layers or a hitherto unidentified phase transition.

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Registry No. $(C_8H_4S_2){\cdot}x^1/_2O_5$, 126457-61-2.

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Lewis Acid Complexation of Polymers: Gallium Chloride Complex of Nylon 6

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We report our concept of using Lewis acid complexation of polymers to modify polymer properties, mediate solubility and processing, and probe intermolecular interactions such as hydrogen bonding.

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