produced only mixtures of these hydride species, even under several different conditions.

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Registry No. Rh(allyl)$_3$, 12082-48-3; TiO$_2$, 13463-67-7; Rh, 7440-16-6.

Supplementary Material Available: Figures 1 and 2 containing binding energy changes of O(2p) and Rh(3d$_{5/2}$) electrons and IR spectra of -O*-Rh(allyl)$_2$ and its thermal derivatives, respectively, and Table I containing UPS, XPS, and IR data (3 pages). Ordering information is given on any current masthead page.

Synthesis of $[(Ph_4P)AgSe_4]_n$. A Novel One-Dimensional Inorganic Polymer

Mercouri G. Kanatzidis* and Song-Ping Huang

Department of Chemistry and Center for Fundamental
Materials Research, Michigan State University
East Lansing, Michigan 48824

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The chemistry of soluble and solid-state metal chalcogenide materials is an area of intense investigation.[1] Interest in this large class of compounds is wide and it derives from their utility in diverse applications such as industrial catalysis,[2] modeling of metalloenzymes,[3] lubricants,[4] rechargeable batteries,[5] nonlinear optics,[6] and electronics.[7] The sulfides are relevant in all these areas, although the selenides and tellurides are more important in nonlinear optics[6] and electronics.[8] This is one of the reasons that the sulfides have been studied considerably more than the corresponding selenides and tellurides. Another important reason, at least in the case of soluble species, is that the corresponding synthetic procedure for Se and Te materials often cannot parallel that of the sulfides. Surprisingly, little transition-metal selenide chemistry has been reported although a few interesting reports have recently appeared in the literature.[9-12] Particularly interesting are the $W_2Se_{10}^{2-}$,[9a,c] $W_2Se_9^{2-}$,[9a,c] and $V_2Se_{13}^{2-}$[9b] species reported by Ibers et al. for which no analogous sulfur chemistry, with respect to the size of Se_x^{2-} ligands present, exists. For reasons that already have been noted,[9] selenide chemistry may not necessarily parallel that of sulfide.

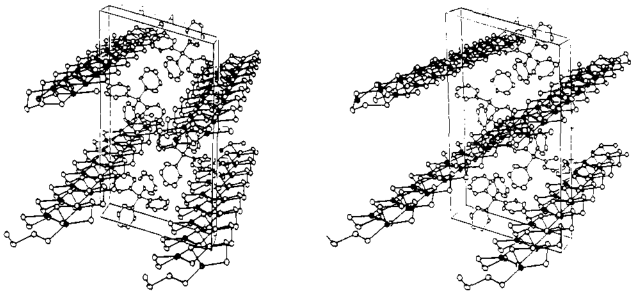

Figure 1. ORTEP representation (stereoview) of the packing arrangement of the $[Ag(Se_4)]_n^{n-}$ chains in the monoclinic lattice. Black circles represent Ag atoms.

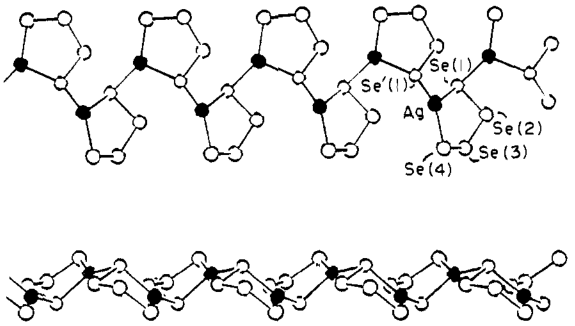

Figure 2. Two views of a $[Ag(Se_4)]_n^{n-}$ chain four unit cells long as drawn by ORTEP with labeling scheme. Black circles represent Ag atoms. Angles about the Ag atom are Se(1)-Ag-Se(1), 114.3 (1)°; Se(1)-Ag-Se(4), 106.6 (1)°; Se'(1)-Ag-Se(4), 138.8 (1)°.

Here we wish to report the synthesis and structural characterization of the new $[Ag(Se_4)]_n^{n-}$, which is the first silver polyselenide. It features an unprecedented low-dimensional polymer structure.

The reaction of $AgNO_3$ with 2 equiv of Na_2Se_5[13] in dimethyl formamide (DMF) solution in the presence of Ph_4PCl followed by filtration and dilution with diethyl ether affords large (up to 2 mm in length) red needles of $[(Ph_4P)AgSe_4]_n$,[14] (I) in 85% yield within several days. Smaller crystals can be obtained overnight with excess diethyl ether. A single-crystal X-ray diffraction analysis[15] reveals that I is composed of noninteracting Ph_4P^+ cations and $[Ag(Se_4)]_n^{n-}$ macroanions. The latter are infinite one-dimensional chains running parallel to the monoclinic *b*-axis. The basic repeating unit is a five-membered $AgSe_4$ ring containing the chelating Se_4^{2-} ligand. Figure 1 represents the packing of the

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[13] Sodium pentaselenide was prepared by the reaction of elemental sodium and selenium in the appropriate ratio in an evacuated Pyrex tube at 450 °C.

[14] Elemental Anal. Calcd for $C_{24}H_{20}PAgSe_4$: C, 37.76; H, 2.62; Ag, 14.14; Se, 41.41. Found: C, 36.89; H, 2.60; Ag, 14.00; Se, 39.36.

[15] Crystal data for $[(Ph_4P)AgSe_4]_n$: monoclinic $P2_1/c$, $Z = 4$, $a = 14.145$ (3) Å, $b = 7.076$ (2) Å, $c = 24.939$ (5) Å, $\beta = 105.23$ (2)°, $V = 2408$ Å^3 at 25 °C. $2\theta_{max}$ (Cu Kα) = 110°. Number of data measured 3505. Number of data having $F_o^2 > 3\sigma(F_o^2)$: 2046. An empirical absorption correction was applied, $\mu = 147$ cm^{-1}. The minimum and maximum transmission was 0.66 and 0.99, respectively. The structure was solved with SHELXS-86 and was refined with the SDP package of crystallographic programs. Final $R = 0.075$ and $R_w = 0.076$.

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$[AgSe_4]_n^{n-}$ chains in the unit cell with the Ph_4P^+ ions acting as spacers. Figure 2 shows two views of an individual chain. Each chain can be thought of as a corrugated ribbon. The mode of polymerization of $AgSe_4$ unit is such that a selenium atom which is coordinated to a Ag atom in the ring also acts as a ligand for a second Ag atom of a neighboring $AgSe_4$ unit. Each $AgSe_4$ ring can be generated from its adjacent one by a 2-fold screw operation parallel to the crystal *b*-axis. The coordination geometry of the Ag atom is trigonal planar with two markedly different intra-ring Ag–Se(1) and Ag–Se(4) bonds of 2.672 (2) and 2.553 (2) Å, respectively, and an inter-ring Ag–Se′(1) bond of 2.545 (2) Å. It is interesting to note the unusual feature of the bridging inter-ring Ag–Se bond being considerably shorter than the corresponding intra-ring bond in the $AgSe_4$ unit. The bonding geometry around the bridging Se(1) atom is trigonal pyramidal. The conformation of the $AgSe_4$ ring is best described as an "envelop" with the Se(2) atom lying 2.21 (4) Å above the Se(1)/Ag/Se(4)/Se(3) plane. The Se–Se distances within the Se_4^{2-} ligand are as follows: Se(1)–Se(2), 2.360 (3); Se(2)–Se(3), 2.339 (3); Se(3)–Se(4), 2.358 (4)Å; and they are similar to those found for $(PPN)_2Se_4{\cdot}4CH_3CN$.[16]

This bridging mode of the Se_4^{2-} ligand in I is uncommon in metal/polychalcogenide chemistry, but it is encountered in the dimeric $[Ag(S_6)]_2^{2-}$,[17] and trimeric $[Cu(S_x)]_3^{3-}$.[18] It is conceivable that the latter two are members of a whole family of compounds with the general formula $[M(Q_x)]_n^{n-}$ (M = group I metals, Q = chalcogen). In this context $[Ag(Se_4)]_n^{n-}$ may be considered an end member. The stabilizaton of polymers via a vis oligomers is probably determined by a combination of counterion and size of the chalcogenide ligands with short chain chalcogenides stabilizing the former. The existence of two other members of this family, the polymeric NH_4CuS_4[19] and $KCuS_4$,[20] is certainly consistent with this contention. It should be noted, however, that the structural motif found in $[(Ph_4P)AgSe_4]_n$ is distinct from that of NH_4CuS_4 or $KCuS_4$ which are composed of double $[Cu(S_4)]_n^{n-}$ chains. In these chains Cu^+ is found in a distorted tetrahedral environment, while the S_4^{2-} units bridge three copper atoms.

The structure of I is unique and has no parallel in chalcogenide chemistry. One-dimensional transition-metal/polychalcogenide compounds such as I are rare, particularly those prepared at ambient temperature. NH_4CuS_4[19] and $(Ph_4P)_2Hg_2Te_5$[21] are two such examples. Other materials containing anionic one-dimensional metal/polychalcogenide chains include $K_4Ti_3S_{14}$[22] and $Na_2Ti_2Se_8$,[23] which feature bridging Q_2^{2-} (Q = S, Se) units.

Preliminary examination of the charge transport[24] and optical[24] properties along the needle axis of single crystals of I indicates wide bandgap/narrow bandwidth semiconducting behavior. A steep optical absorption threshold occurs at 384 nm suggesting a bandgap of 3.2 eV.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles of all atoms (9 pages); a listing of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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Catalysis of Closed-Shell Reactions by Complexation with Metal Radical Cations

Timothy Clark

Institut für Organische Chemie der
Friedrich-Alexander-Universität Erlangen-Nürnberg
Henkestrasse 42, D-8520 Erlangen
Federal Republic of Germany

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One-electron oxidation of organic substrates is one of the few physical processes that can produce similar rate accelerations to those found in enzymatic systems. Bauld,[1] Haselbach,[2] Roth,[3] and Dinnocenzo,[4] among others, have demonstrated this for a variety of Woodward–Hoffmann-type reactions. Ab initio molecular orbital calculations[5] have been widely used to investigate these reactions. The electronic flexibility gained by the presence of a singly occupied orbital often leads to low activation energies, as found in many neutral radical reactions,[6] and the inclusion of a positive charge, which favors one- and three-electron bonding,[7] often leads to even more facile reactions. This latter effect was recently demonstrated theoretically for the addition of the methyl radical to ethylene.[8] The calculated barrier is lowered significantly by complexation of the olefin with the lithium cation, an effect that is expected to be general for radical reactions involving odd-electron bonds in the transition state.[9] However, this catalysis by complexation with a metal cation is not limited to introducing charge into a radical reaction. In principle, it is also possible to introduce both charge and radical character into a closed-shell reaction by complexation with a doublet metal cation. This communication reports model ab initio molecular orbital calculations[10,11] designed to test this hypothesis.

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