± 2 M^{-1} s^{-1} and $(k_{\mathrm{stoich}})_b = 22 \pm 2$ s^{-1}].

The mechanism of catalytic sulfur dioxide autoxidation must accommodate several factors: (1) the products of both the stoichiometric and catalytic reactions are sulfate; (2) a bifurcation exists between stoichiometric and catalytic reactions at the point of dioxygen entry; (3) both stoichiometric and catalytic reactions display essentially identical rate equations. Equations 3, 5, and 6 or eqs 3, 5, 7, and 8 both represent plausible pathways, with the generation of the sulfite radical (eq 3) as the rate-limiting step. This contrasts the previous mechanisms for S(IV) autoxidation implicating sulfite radicals as the chain carriers.[1b] In the present study, a "well-behaved" [Ni^{III}(cyclam)] chain carrier mechanism is a more tenable explanation of the concordant catalytic and stoichiometric rate equations and respective rate constants.[22] The catalysis of these reactions by chloride and bromide is now under study.[23]

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Supplementary Material Available: Tables of stoichiometries (Tables 1 and 2) and kinetic data (Tables 3-6) (4 pages). Ordering information is given on any current masthead page.

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Organotelluride Chemistry: An Unusual Free Organotelluride Anion and the Metal Complex $[\mathrm{Ag_4(TeR)_6}]^{2-}$ (R = Thienyl)

The complexation chemistry of organothiolate ligands is under intense investigation,[1] not only because of their relevence to biological and catalytic applications but also because of their extraordinarily rich structural diversity.[2] The molecules not only extend our knowledge of new structural types but also provide precursors to extended polymeric compounds[3] and new sulfide clusters.[4] In contrast, the chemistry of the organoselenides and organotellurides is much less developed.[5] In fact, to our knowledge, only one other homoleptic metal organotelluride has been structurally characterized.[6] This is surprising because organothiolate complexes form an almost limitless variety of structures deriving from only subtle changes in electronic and steric factors of the organic group.[7]

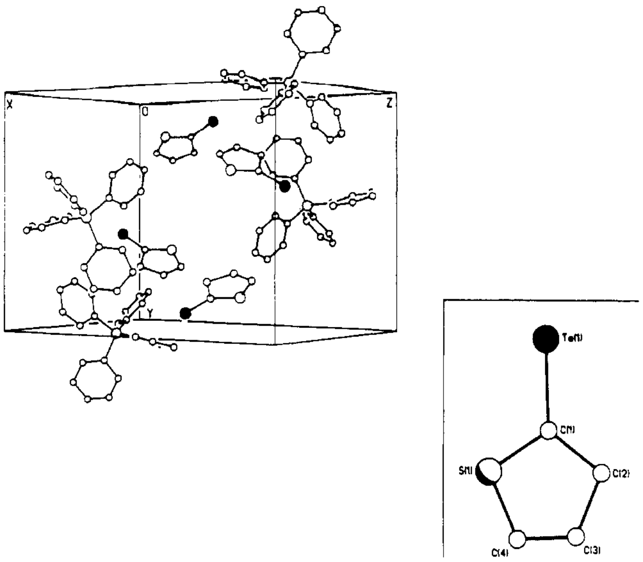

Figure 1. Thermal ellipsoid plot of the unit cell of $[(C_6H_5)_4P][C_4H_3STe]$ showing the isolated anion I. The inset shows the tellurothiophene anion in detail. Some significant distances for molecule I (Å): Te(1)–C(1) = 2.06 (2), S(1)–C(1) = 1.67 (2), S(1)–C(4) = 1.66 (3), C(1)–C(2) = 1.55 (2), C(2)–C(3) = 1.54 (3), C(3)–C(4) = 1.35 (4). Some significant bond angles (deg): C(1)–S(1)–C(4) = 100 (1), Te(1)–C(1)–S(1) = 122 (1), Te(1)–C(1)–C(2) = 129 (1), S(1)–C(1)–C(2) = 108 (1), C(1)–C(2)–C(3) = 105 (2), C(2)–C(3)–C(4) = 115 (2), S(1)–C(4)–C(3) = 111 (2).

In this paper, we report the preparation and structural characterization of a free organotelluride and its use in preparation of a tetranuclear silver cluster. This represents the first member of a potentially huge class of new metal organochalcogenide complexes.

We have recently been investigating the chemistry of transition-metal selenide and telluride complexes.[8] We hope to extend this chemistry by using metal organotelluride and -selenide complexes as starting materials for the preparation of binary compounds, a technique that has worked very well for metal sulfide synthesis.[4] In fact, a recent report describes the preparation of a tellurocubane cluster of iron using $[(\mathrm{PhTe})_4\mathrm{Fe}]^{2-}$ as a starting material.[9] In addition, the use of metal organochalcogenides to generate new solids has recently been reported.[10] Thus it was felt that exploration of metal organotelluride chemistry would yield novel coordination compounds as well as suitable precursors for new metal telluride clusters.

The reported difficulties in isolating crystalline phenyltelluride complexes[11] led us to consider other organotellurides. We were attracted to the report by Engman and Cava[12] of the stability of the di-2-thienyl ditelluride, as well as the high nucleophilicity of its corresponding anion, 2-tellurothiophene. Surprisingly, we found that the parent anion could be readily isolated in good yield, in straightforward fashion by using tetraphenylphosphonium as a counterion. Deprotonation of thiophene with butyllithium results exclusively in 2-lithiothiophene. Reaction of this anion with elemental tellurium generates the 2-tellurothiophene anion, as described by Cava. If, instead of oxidation, $(C_6H_5)_4PBr$ is added, large orange crystals of the salt can be isolated in good yield upon slow addition of diethyl ether. The salt $[(C_6H_5)_4P][C_4H_3STe]$ was characterized by IR spectroscopy, elemental analysis[13] and

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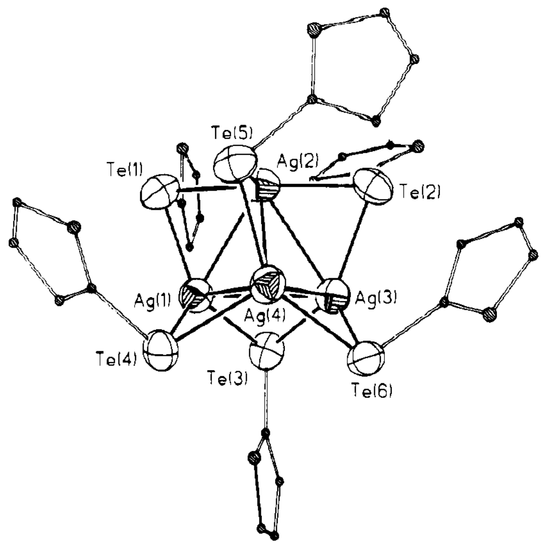

Figure 2. Thermal ellipsoid plot (50% thermal ellipsoids for cluster atoms; thiophene groups represented as spheres) of $[Ag_4(TeR)_6]^{2-}$ where R = tellurothiophene. The average Ag–Te bond distance is 2.754 (5) Å, ranging from 2.735 (5) to 2.802 (5) Å. The average direct Ag–Ag distance is 3.13 (9) Å, ranging from 3.013 (5) to 3.230 (5) Å. The Ag–S distances are all greater than 3.7 Å and are clearly noninteracting. The Te–C distances average 2.17 (8), ranging from 2.07 (4) to 2.28 (4) Å.

single-crystal X-ray diffraction.[14]

The X-ray diffraction analysis reveals that the organotelluride anion is well separated from the corresponding tetraphenylphosphonium cation in the unit cell. (See Figure 1.) The closest interaction involving non-hydrogen atoms between the two ions is 4.01 (1) Å (Te1···C36). In addition, there does not appear to be any solvent molecules or lithium cations in the unit cell to stabilize the anion. The C–Te bond distance is 2.06 (2) Å, which is relatively short. The sum of covalent radii is 2.14 Å,[15] and most characterized Te–C bonds are approximately that length. (E.g., Te–C is 2.13 Å in $Te_2(p\text{-}CH_3C_6H_4)_2$.[16])

The preparation of isolated organoelement anions of the type R_nE^- has been under active investigation. Some elegant recent work has provided several examples of salts where anions of oxygen, nitrogen, phosphorus, arsenic, and antimony have been isolated.[17] These usually involve the use of crown ethers to encapsulate an alkali-metal cation or electron-withdrawing groups on the R group[18] to stabilize the anion. The heavier cogeniers of group 16 have not been as extensively investigated. Several lithium thiolates have been reported, but they contain substantial amounts of ion pairing between Li^+ and the thiolate anion.[19] The origin of the unusual stabilization of molecule I is not clear but probably is caused by the electronegative heteroatom in the aromatic ring. This would withdraw electron density into the aromatic framework more efficiently than a simple phenyl ring. This idea is supported by the short Te–C bond, which suggests a small amount of multiple bonding.

The increased stability of the organotelluride augurs well for its use as a ligand with metals. Indeed, it reacts cleanly with a solution of silver nitrate dissolved in DMF to yield the new cluster $[Ag_4(TeR)_6]^{2-}$. The molecule can be isolated in reasonable yield by using tetraphenylphosphonium as a counterion. The salt $[(C_6H_5)_4P]_2[Ag_4(TeC_4H_3S)_6]$ was characterized by elemental analysis, IR spectroscopy,[20] and single-crystal X-ray diffraction.[21]

The crystal structure reveals two well-separated cations and the tetrameric silver cluster dianion. The heavy atom framework is analogous to the structures of $[Cu_4(SMe)_6]^{2-}$[22] and $[Cu_4(SPh)_6]^{2-}$,[22,23] which consist of tetrahedra of metal atoms edge bridged by organochalcogen ligands. This creates an octahedron of tellurium atoms inscribed by a tetrahedron of silver atoms (see Figure 2). The Ag–Te distances range from 2.727 (5) to 2.807 (5) Å. The Ag–Ag distances average 3.13 (9) Å, which is long compared to the distance in elemental silver (2.88 Å).[24] The overall coordination environment around each silver atom is trigonal planar, and the Ag–Te–Ag angles are acute (69 (2)° average) (see Figure 3 in supplementary material).

It is possible for the thiophene ring to be involved in inter- or intramolecular interaction with the silver atoms by analogy with a reported silver pyridinethiolate complex.[25] However, we were surprised to find that the sulfur atom does not appear to be involved in any interaction with silver atoms. It should be noted that the sulfur atoms are disordered over the two possible sites in several of the thiophene rings and the rings are somewhat disordered themselves. This contributes to a somewhat high *R* factor but does not appear to have any effect on the overall structure.[26]

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(13) All reactions were performed under purified argon by using standard Schlenk techniques and solvents dried by standard methods. A solution of 0.30 mL (3.8 mmol) of thiophene in 10 mL of THF was cooled to −78 °C, and 2.8 mL (6.4 mmol) of *n*-BuLi was added via syringe. The mixture was stirred for 15 min and warmed to room temperature, followed by addition of 0.50 g (3.9 mmol) of powdered tellurium. The mixture was stirred for 30 min and filtered and 10 mL of an acetonitrile solution containing 0.7 g of $(C_6H_5)_4PBr$ was added. The dark red solution was filtered and layered with 10 mL of hexane and stored at 4 °C overnight, generating 0.64 g (70% yield) of red-orange crystals of the product. Anal. Calcd for $C_{28}H_{23}PSTe$: C, 61.20; H, 4.04. Found: C, 60.11; H, 4.10.

(14) An orange crystal was sealed in epoxy and mounted on a Nicolet R3/mV diffractometer. A unit cell was obtained from 36 well-centered reflections. Crystal data: monoclinic space group, $P2_1/n$, a = 10.752 (5) Å, b = 13.745 (8) Å, c = 17.358 (8) Å, β = 108.06 (4), V = 2439 (2) Å^3, Z = 4. Data were collected in the range 3.5° ≤ 2θ ≤ 45° and an absorption correction was performed using the ψ-scan technique. The structure was solved by direct methods, and least-squares refinement of all non-hydrogen atoms performed anisotropically, with fixed hydrogen atoms on the phenyl groups, using 1268 observed reflections of $I > 3\sigma(I)$, resulted in an agreement of R = 0.0545 and R_w = 0.0643.

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(20) A solution of 0.15 mL (1.9 mmol) thiophene in 10 mL of THF was cooled to −78 °C and 1.3 nL (3 mmol) of *n*-BuLi was added via syringe. The mixture was stirred for 15 min and allowed to warm to room temperature. Tellurium powder (0.25 g, 2.0 mmol) was added with stirring. The mixture was filtered after 20 min, producing a clear yellow solution. A solution of 0.17 g (1.00 mmol) of $AgNO_3$ in 10 mL of CH_3CN was added via syringe. After the mixture was stirred overnight, a 10-mL acetonitrile solution of 0.37 g of $(C_6H_5)_4PBr$ was added via syringe. The yellow solution was filtered through Celite and the volume reduced by half under vacuum. The solution was layered with 5 mL of diethyl ether and stored overnight at 4 °C, generating yellow crystals, which were washed with fresh ether and dried, yielding 0.418 g (yield 61%) of pure product. Anal. Calcd for $C_{72}H_{58}Ag_4P_2S_6Te_6$: C, 36.40; H, 2.47. Found: C, 37.07: H, 2.74.

(21) A yellow crystal was prepared as described above and treated as in ref 14. Crystal data: orthorhombic space group, $P2_12_12_1$, a = 13.768 (4) Å, b = 24.276 (7) Å, c = 25.183 (6) Å, V = 8417 (3) Å^3, Z = 4. The data were corrected for absorption by using the ψ-scan technique. The structure was solved by direct methods and refined by using least-squares programs from the standard Nicolet package. The heavy atoms Te, Ag, and P were refined anisotropically, while the atoms of the thiophene rings were refined isotropically and the carbon atoms of the counterions were refined as rigid groups (see ref 26). The refinement of 3256 observed reflections ($I > 3\sigma(I)$) with 281 parameters converged at R = 0.0689 and R_w = 0.0745. An identical refinement with the coordinates of the model inverted converged with R = 0.0698 and R_w = 0.0987.

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(26) See supplementary material for a complete description of the disorder problem in molecule II and attempts to resolve it.

In conclusion, we report the isolation of the unusual RTe– anion where R is thienyl, which may be the first member of a large class of stable anions. This can be used to prepare a new silver telluride cluster $[Ag_4(TeR)_6]^{2-}$, which is only the second homoleptic metal organotelluride structurally characterized.

Acknowledgment. The support of the National Science Foundation (Grant CHE-8802217) is gratefully acknowledged.

Supplementary Material Available: Complete listings of crystallographic information, atomic coordinates and isotropic thermal parameters, bond distances and angles, anisotropic thermal parameters, and coordinates of hydrogen atoms for compounds I and II, another view of molecule II, and a complete description of the disorder problem in molecules I and II and the attempts made to resolve it (14 pages); listings of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Mixed-Metal Alkoxides $[((L_2)Rh)_2Sn(OEt)_6]$, Where L_2 = 1,5-Cyclooctadiene (COD) (3) and $(CO)_2$ (4), and the Conversion of 3 to Rh and SnO_2 under Mild Conditions

There has been growing interest in the marriage of classical organometallic and inorganic chemistry for the synthesis of soluble molecular species as models for late-transition-metal catalysts on metal oxide supports.[1] In one approach, a variety of polyoxoanion-supported organometallic fragments have been prepared.[2] However, less attention has been directed toward the design of new chemical routes for the preparation of supported catalysts themselves.[3] An example of the existing routes to these catalysts is given as follows:[3a]

$$Ti(O\text{-}i\text{-}Pr)_4 + NaOH \xrightarrow[2.\ H_2O]{1.\ MeOH} NaTi_2O_5H \xrightarrow[-2Na^+]{+Ni^{2+}} Ni[Ti_2O_5H]_2 \xrightarrow{\text{reduction}} \text{Ni on } TiO_2 \quad (1)$$

As part of our strategy to prepare new mixed-metal alkoxide compounds[4] containing a catalytically important transition metal,

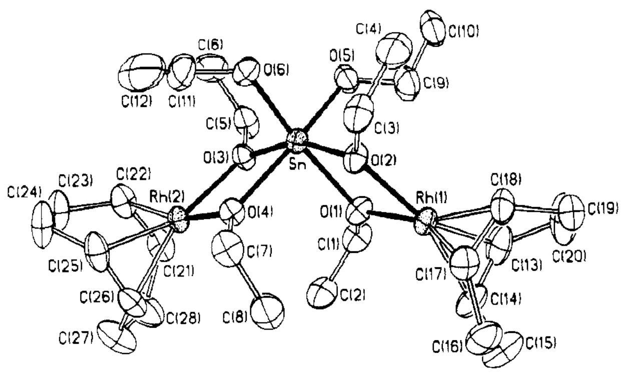

Figure 1. ORTEP plot of $[((COD)Rh)_2Sn(OEt)_6]$, showing the atom-numbering scheme. Relevant bond distances (Å): Rh(1)–O(1) = 2.059 (4), Rh(1)–O(2) = 2.082 (4), Rh(2)–O(3) = 2.063 (5), Rh(2)–O(4) = 2.065 (4), Sn–O(1) = 2.098 (3), Sn–O(2) = 2.075, Sn–O(3) = 2.082 (4), Sn–O(4) = 2.103 (4), Sn–O(5) = 1.979 (5), Sn–O(6) = 1.980 (4), Rh(1)–C = 2.080 (6) (average), Rh(2)–C = 2.078 (average). Relevant bond angles (deg): O(1)–Rh–O(2) = 74.4 (1), O(3)–Rh(2)–O(4) = 74.6 (2), O(1)–Sn–O(2) = 73.7 (1), O(3)–Sn–O(4) = 73.4 (2), O(5)–Sn–O(6) = 90.4 (2).

we report here the synthesis and characterization of the new rhodium–tin alkoxide compounds $[(L_2(Rh))_2Sn(OEt)_6]$, where L_2 = 1,5-cyclooctadiene (**3**) and $(CO)_2$ (**4**), and the conversion of **3** to Rh and SnO_2.

The addition of 1 equiv of (cyclooctadiene)rhodium(I) chloride dimer[5] to $[Tl_2Sn(OEt)_6]$[4a] in THF at room temperature results in smooth precipitation of thallium(I) chloride, according to eq 2.[6] After filtration, removal of the volatile components in vacuo,

$$\underset{\mathbf{1}}{[Tl_2Sn(OEt)_6]} + \underset{\mathbf{2}}{[(COD)RhCl]_2} \rightarrow \underset{\mathbf{3}}{[((COD)Rh)_2Sn(OEt)_6]} + 2TlCl \quad (2)$$

extraction, and crystallization from *n*-pentane at −30 °C, pale yellow crystals that analyzed correctly as $[((COD)Rh)_2Sn(OEt)_6]$ (**3**) were isolated in 90.8% yield.[7] In toluene-d_8 solution at room temperature, **3** exhibits only one type of ethoxide and cyclooctadiene ligand, as determined by ^1H and ^{13}C NMR spectroscopy. Upon cooling, however, the ^1H NMR ethoxide ligand resonances begin to broaden at 233 K, and the cyclooctadiene resonances begin to broaden at 193 K. Unfortunately, temperatures low enough to freeze out the exchange process could not be reached, so the thermodynamically preferred conformation of this com-

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(6) To a solution of 2.0 g (2.5 mmol) of $[Tl_2Sn(OEt)_6]$ in THF was added a THF solution of 1.24 g (2.5 mmol) of $[(COD)RhCl]_2$ with rapid stirring. A white precipitate was immediately formed. After being stirred for 2 h, the solution was filtered, and the volatile components were removed in vacuo to give a yellow oil, which was taken up in *n*-pentane. The resultant solution was filtered and evaporated to dryness to give a pale yellow solid. Recrystallization from *n*-pentane at −30 °C gave crystals suitable for X-ray diffraction.

(7) $[((COD)Rh)_2Sn(OEt)_6]$: mp 82–84 °C; ^1H NMR (C_6D_6, 20 °C, 250 MHz) 3.97 (q, 7 Hz, $^2J_{^{119}Sn-^1H}$ = 52 Hz, 12 H, OCH_2CH_3), 3.69 (s, br, 4 H, $-CH{=}CH-$), 2.17 (m, 4 H, $=CH-CH_2-$), 1.59 (t, 18 H, OCH_2CH_3), 1.41 ppm (m, 4 H, $=CH-CH_2-$); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 62.9 MHz) 73.9 (d, $^1J_{^{103}Rh-^{13}C}$ = 15 Hz, $-CH{=}CH-$), 60.9 (s, $^2J_{^{119}Sn-^{13}C}$ = 27 Hz, OCH_2CH_3), 30.6 (s, $=CH-CH_2-$), 20.8 ppm (s, $^3J_{^{119}Sn-^{13}C}$ = 16 Hz); ^{119}Sn NMR (C_6D_6, 20 °C, 93.3 MHz) −529.5 ppm (s); IR (KBr disk) 2951.7 (s), 2878.0 (s), 1471.0 (m), 1435.0 (m), 1380.4 (s), 1299.0 (m), 1153.0 (m), 1089.5 (s), 1033.0 (s), 961.3 (m), 884.1 (s), 840.1 (s), 558.2 (s), 452.1 (s), 540.0 (s), 525.9 (s), 498.0 cm^{-1} (s). Anal. Calcd for $C_{28}H_{54}O_6Rh_2Sn$: C, 41.46; H, 6.71. Found: C, 41.76; H, 6.96 (monomeric in benzene solution).

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