Figure 1. ORTEP view of {Cp$_2$Sc[μ-O$_2$CSi(SiMe$_3$)$_3$]}$_2$ (3) with thermal ellipsoids drawn at the 20% probability level.

3 result in isolation of samples containing small amounts of an additional product, 5.[7] Compound 5 could not be isolated in pure form, but ^{1}H NMR spectroscopy shows that Cp and Si(SiMe$_3$)$_3$ groups are present in a 2:1 ratio. It therefore seemed that 5 could be formulated as a siloxide, [Cp$_2$ScOSi(SiMe$_3$)$_3$]$_x$, generated by expulsion of CO from 3. Analogous CO elimination reactions have been observed for the esters (Me$_3$Si)$_3$SiCO$_2$R (R = Me, SiPh$_3$, SiMe$_3$, Si(SiMe$_3$)$_3$),[6] and for the copper(II) complexes Cu(O$_2$CSiR$_3$)$_2$·H$_2$O (SiR$_3$ = SiPh$_3$, SiMePh$_2$, SiMe$_2$Ph, SiPh$_2$SiPh$_3$).[14] Consistent with this, reaction of 1 with ^{13}CO$_2$ produced a mixture of 3-^{13}C and 5, and no incorporation of carbon-13 into 5 could be detected (by ^{13}C NMR spectroscopy). However, 3 does not decompose to a measurable extent when heated to 95 °C for 60 h (by ^{1}H NMR, benzene-d_6). We are therefore reluctant at this time to definitely assign a structure to 5.

Supplementary Material Available: Details concerning the structure solution and refinement and tables of crystal data, data collection, and refinement parameters, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and their isotropic thermal parameters (9 pages); listings of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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Catalysis of the Autoxidation of Aqueous Sulfur Dioxide Using [Ni^{III}(cyclam)]: Evidence for a Novel Radical Chain Mechanism

Sulfur dioxide is a menace to the environment, and transition-metal-catalyzed autoxidation offers a potentially cost-effective means for its abatement.[1] Aqueous catalyst solutions have been
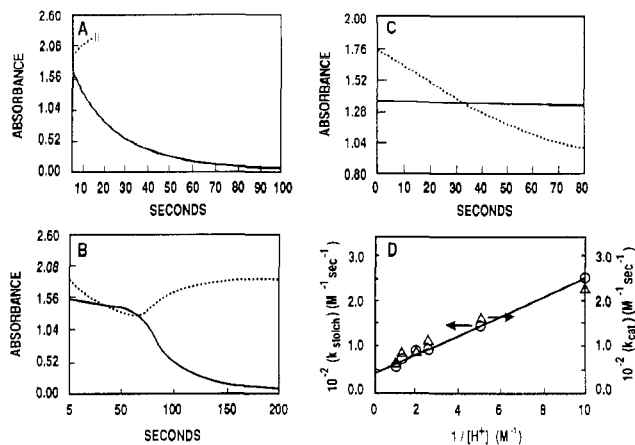

Figure 1. Temporal profiles (A–C: (- -) λ = 206 nm; (—) λ = 308 nm; path length = 1 cm) and kinetic comparison (D) of stoichiometric oxidation and catalytic autoxidation of excess S(IV) using [(cyclam)Ni^{III}] (T = 25 °C). (A) Pseudo first-order rate behavior for stoichiometric reaction {p_{Ar} ~ 101 kPa [HBF$_4$] = 1.0 M; [(cyclam)Ni^{III}]$_0$ = 1.4 × 10^{-4} M; [S(IV)]$_0$ = 5.0 × 10^{-4} M}. (B) Reaction under deficiency of dioxygen {p_{O_2} ~ 21 kPa; [HBF$_4$] = 1.0 M; [(cyclam)Ni^{III}] = 1.2 × 10^{-4} M; [S(IV)] = 1.0 × 10^{-3} M}. (C) Reaction under excess dioxygen {p_{O_2} ~ 450 kPa; [HClO$_4$] = 1.0 M; [(cyclam)Ni^{III}]$_0$ = 1.2 × 10^{-4} M; [S(IV)]$_0$ = 1.0 × 10^{-3} M}. (D) Comparison between rate constants for the stoichiometric reaction of [(cyclam)Ni^{III}] with S(IV) and the [(cyclam)-Ni^{III}]-catalyzed autoxidation of S(IV) in aqueous perchloric acid {[(cyclam)Ni^{III}]$_0$ = 1.2 × 10^{-4} M; [S(IV)]$_0$ = 1.0 × 10^{-3} M; μ = 1.0 M (LiClO$_4$)}: (O) stoichiometric reaction; ($\triangle$) catalytic reaction.

described with pH > 1.5 using iron,[2,3] manganese,[3] cobalt,[4] and copper[5] species. [Ni^{III}(cyclam)] was selected as an oxidant (E^0 ~ 0.96 V) and found to exhibit distinctive catalytic properties in this regard.[6] Two equivalents of [Ni^{III}(cyclam)] were consumed per equivalent of S(IV) in acidic (pH < 1) anaerobic solutions to produce 2 equiv of [Ni^{II}(cyclam)] and 1 equiv of S(VI).[10] Oxygenated solutions furnished the catalytic output of sulfate.[11] Kinetic evidence is presented now for a novel mechanism of sulfur dioxide autoxidation with [Ni^{III}(cyclam)] serving as the radical chain carrier.

Analogous reactions in 1.0 M acid under either argon or dioxygen have been monitored spectroscopically to determine the relationship between the stoichiometric and catalytic reactions. Wavelengths of 206 and 308 nm were chosen to follow [Ni^{III}-(cyclam)] (ϵ_{206} = 2800 M^{-1} cm^{-1}; ϵ_{308} = 11 070 M^{-1} cm^{-1}), [Ni^{II}(cyclam)] (ϵ_{206} = 10 200 M^{-1} cm^{-1}; ϵ_{308} = 17 M^{-1} cm^{-1}), and

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(6) Cyclam is 1,4,8,11-tetraazacyclotetradecane and is otherwise referred to as [14]aneN$_4$. The preparation of [Ni^{III}(cyclam)(Cl)$_2$](ClO$_4$) at 0 °C was a modification of ref 7. Aquation of the dichloro complex according to the procedure of ref 8 gave the complex ion [Ni^{III}(cyclam)] or [Ni^{III}(cyclam)(H$_2$O)$_2$]$^{3+}$ (λ_{max} = 308 nm; ϵ_{max} = 11 070 ± 95 M^{-1} cm^{-1}).[9]
(7) Gore, E. S.; Busch, D. H. *Inorg. Chem.* **1973**, *12*, 1–3.
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(10) See the supplementary data, Tables 1 and 2, for the stoichiometric and catalytic stoichiometries, respectively.
(11) Reaction of a solution containing initially 1.0 × 10^{-4} M [Ni^{III}(cyclam)] and 0.10 M HCl to which 0.10 M S(IV) was added (slowly) under p_{O_2} ~ 260 kPa led to the complete conversion of S(IV) to S(VI) [isolated as Na$_2$SO$_4$ from solution adjusted to pH 8; IR (KBr) ν = 1130 br s, 720 s cm^{-1}] with [(cyclam)Ni^{III}(Cl)(H$_2$O)]$^{2+}$ remaining spectroscopically unchanged (ϵ_{308} ~ 13 700 M^{-1} cm^{-1}). Absence of dithionate (S$_2$O$_6^{2-}$) absorptions (ν = 1245 s, 1000 s cm^{-1}) requires it to be <2%.

aqueous sulfur dioxide (ϵ_{206} = 1800 M^{-1} cm^{-1}; ϵ_{308} = 57 M^{-1} cm^{-1}).[12] Figure 1A–C illustrates the time-dependent behavior of absorbances at these wavelengths under conditions where [Ni^{III}(cyclam)] is in large deficiency relative to aqueous sulfur dioxide with p_{O_2} = 0, 21, and 450 kPa, respectively.
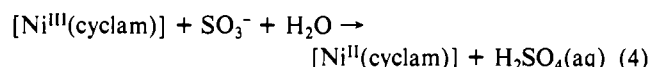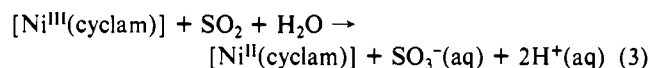
The anaerobic reaction in Figure 1A displays monophasic exponential profiles corresponding to the consumption of the deficient [Ni^{III}(cyclam)] at 308 nm and the concomitant production of [Ni^{II}(cyclam)] at 206 nm. Specific pseudo-first-order rate constants were obtained from such curves (λ = 308, 408, or 422 nm) pertaining to the stoichiometric reaction.[13] Reactions performed with either [Ni^{III}cyclam]$_0$ or [S(IV)]$_0$ in >7-fold deficiency were found to adhere to eq 1.[15]

$$\frac{-d[Ni^{III}(cyclam)]}{dt} = -2\frac{d[S(IV)]}{dt} = 2(k_{stoich})[S(IV)][Ni^{III}(cyclam)] \quad (1)$$

Acidity dependence over the perchloric acid concentration range 0.10–1.0 M [μ = 1.0 M (LiClO$_4$)] (Table 5, Supplementary Data) demonstrates that S(IV) oxidation by [Ni^{III}(cyclam)] features both parallel protonated and deprotonated pathways (eq 2). In

$$-\frac{1}{2}\frac{d[Ni^{III}(cyclam)]}{dt} = \frac{-d[S(IV)]}{dt} = \{(k_{stoich})_a + (k_{stoich})_b/[H^+]\}[S(IV)][Ni^{III}(cyclam)] \quad (2)$$

eq 2 $(k_{stoich})_a$ and $(k_{stoich})_b$ have values of 37 ± 2 M^{-1} s^{-1} and 22 ± 2 s^{-1}, respectively. Both redox species have acidity quotients (pK_a[Ni([cyclam)(H$_2$O)$_2^{3+}$] ~ 3.5 and pK_a[SO$_2$(aq)] = 1.4), and the equivalent kinetic expressions are not resolved in the deprotonated situation.[16,17] The protonated pathway is assigned unambiguously to the homogeneous oxidation of aqueous SO$_2$ to aqueous hydrogen sulfate and sulfuric acid.

$$[Ni^{III}(cyclam)] + SO_2 + H_2O \rightarrow [Ni^{II}(cyclam)] + SO_3^-(aq) + 2H^+(aq) \quad (3)$$

$$[Ni^{III}(cyclam)] + SO_3^- + H_2O \rightarrow [Ni^{II}(cyclam)] + H_2SO_4(aq) \quad (4)$$

Possibility of sulfite radical protonation to form HSO$_3$ in eqs 3 and 4 remains open and currently is under investigation.[18]

Other analogous reactions equilibrated under dioxygen, Figure 1B,C, displayed drastic deviations from first-order behavior. The solution equilibrated with just 21 kPa of dioxygen gave rise to an induction period in [Ni^{III}(cyclam)] consumption (Figure 1B) that is absent in either the anaerobic solution (Figure 1A) or the solution under 450 kPa of dioxygen (Figure 1C). Decay profiles arise at 206 nm for the oxygenated solutions (Figures 1C and 1B), whereas in deoxygenated solutions only [Ni^{II}(cyclam)] production was observed.
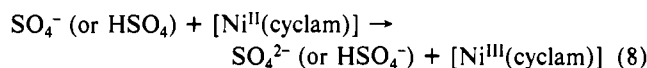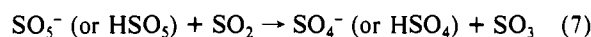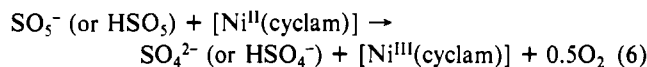
Figure 1B displays a picture consistent with radical scavenging by dioxygen, in particular, the characteristics of the 206- and 308-nm curves. At the minimum of the 206-nm curve Δ[S(IV)] = ΔA/$\epsilon_{206}^{S(IV)}$ = 3 × 10^{-4} M. Subsequent to dioxygen depletion, the consumption of [Ni^{III}(cyclam)] occurs, though nonexponen-

tially, due to some remaining autoxidation from a trace (<1.5 × 10^{-4} M) of dioxygen remaining in the solution. Solutions as in Figure 1C, maintained under excess dioxygen, show only decay profiles at 206 nm. The constant [Ni^{III}(cyclam)] absorbance at 308 nm points to a catalytic cycle for the autoxidation of S(IV) in which [Ni^{III}(cyclam)] is regenerated rapidly from [Ni^{II}(cyclam)].

A bifurcation at the point of dioxygen entry can be attributed to reaction 5 where dioxygen scavenges the sulfite radical to form the peroxysulfate radical.[19] Rapid regeneration of [Ni^{III}(cyclam)]

$$SO_3^- + O_2 \xrightarrow{k = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}} SO_5^- \text{ (or HSO}_5) \quad (5)$$
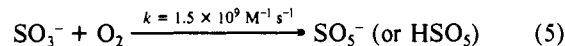
is accomplished in a kinetically invisible follow up step by an oxysulfur radical species, either as in eq 6 or eqs 7 and 8.

$$SO_5^- \text{ (or HSO}_5) + [Ni^{II}(cyclam)] \rightarrow SO_4^{2-} \text{ (or HSO}_4^-) + [Ni^{III}(cyclam)] + 0.5O_2 \quad (6)$$

$$SO_5^- \text{ (or HSO}_5) + SO_2 \rightarrow SO_4^- \text{ (or HSO}_4) + SO_3 \quad (7)$$

$$SO_4^- \text{ (or HSO}_4) + [Ni^{II}(cyclam)] \rightarrow SO_4^{2-} \text{ (or HSO}_4^-) + [Ni^{III}(cyclam)] \quad (8)$$

Confirmation of the sulfate produced was obtained by infrared spectroscopy (ν = 1130, 625 cm^{-1}). Both eq 6 and eqs 7 and 8 are consistent with the absence of peroxysulfate in the catalyst solutions.[20]

To measure the kinetics of the catalysis, plots of absorbance against time, such as Figure 1C, were obtained and an initial (linear) rate of absorbance decay for S(IV) was calculated. From those data, it was possible to calculate a specific pseudo-zero-order rate constant or turnover frequency for the catalysis.

$$\text{turnover freq} = \frac{-d[S(IV)]}{dt}\frac{1}{[Ni^{III}(cyclam)]} = \frac{-dA^{S(IV)}}{dt}\frac{1}{\epsilon^{S(IV)}[Ni^{III}(cyclam)]} \quad (9)$$

Reactions were measured encompassing concentrations 1.4 × 10^{-4} M > [Ni^{III}(cyclam)]$_0$ > 7.8 × 10^{-6} M, 0.018 M > [S(IV)]$_0$ > 0.0010 M, and 450 kPa > p_{O_2} > 21 kPa with both [S(IV)]$_0$ and [O$_2$]$_0$ in large excess. The calculated specific second-order rate constant in 1.0 M perchloric acid of k_{cat} = 58 ± 8 M^{-1} s^{-1} was found to be independent of dioxygen concentration (eq 10).[21] This

$$k_{cat} = \frac{-d[S(IV)]}{dt}\frac{1}{[S(IV)][Ni^{III}(cyclam)]} = \frac{\text{turnover freq}}{[S(IV)]} \quad (10)$$

specific rate constant is the same as that for the analogous stoichiometric reaction, k_{stoich} = 54 ± 5 M^{-1} s^{-1}. Other distinct similarities arise when the catalytic reaction is measured over a range of acidities, 1.0 M > [H$^+$] > 0.10 M. Figure 1D shows that specific second-order rate constants for the stoichiometric and catalytic reactions plotted against 1/[H$^+$] dictate an essentially equivalent rate law for these processes (eqs. 2 and 11).[21] A

$$\frac{-d[S(IV)]}{dt} = (k_{cat})[S(IV)][Ni^{III}\text{cyclam}]$$
$$= \{(k_{cat})_a + (k_{cat})_b/[H^+]\}[S(IV)][Ni^{III}\text{cyclam}] \quad (11)$$

common slope and intercept for stoichiometric and catalytic reactions is demonstrated by Figure 1D. Hence, second-order rate constants for the protonated and deprotonated pathways agree [$(k_{cat})_a$ = 41 ± 7 M^{-1} s^{-1} and $(k_{cat})_b$ = 21 ± 3 s^{-1}; $(k_{stoich})_a$ = 37

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(13) Methods used for obtaining pseudo-first-order rate constants are found in ref 14. Agreement was generally better than ±6% between identical runs employing different sets of stock solutions.

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(15) See supplementary data, Tables 3 and 4.

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(17) Martell, A. G.; Sillen, L. G. *Stability Constants*; Special Report 17; The Chemical Society: London, 1964; p 230.

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(21) See supplementary data, Table 6.

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

Acknowledgment. We gratefully acknowledge informative discussions with Professors R. N. Bose, E. S. Gould, D. W. Margerum, and D. M. Stanbury. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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 [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]

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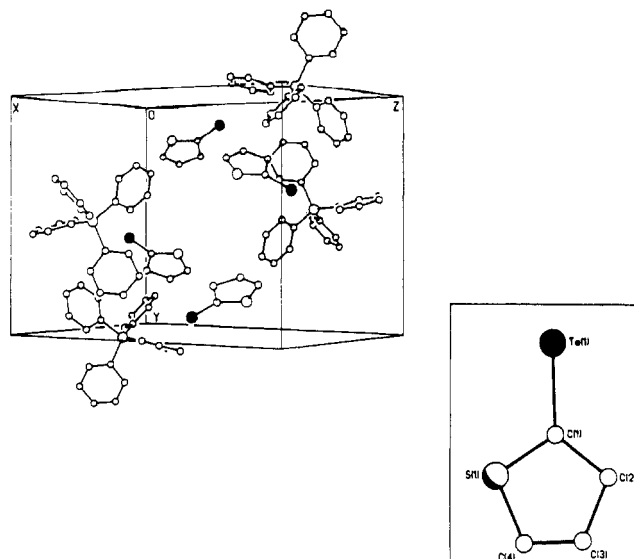(6) Behrens, U.; Hoffmann, G.; Klar, G. *Chem. Ber.* **1977**, *110*, 3672.

Figure 1. Thermal ellipsoid plot of the unit cell of [(C$_6$H$_5$)$_4$P][C$_4$H$_3$STe] 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 [(PhTe)$_4$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$_6$H$_5$)$_4$PBr is added, large orange crystals of the salt can be isolated in good yield upon slow addition of diethyl ether. The salt [(C$_6$H$_5$)$_4$P][C$_4$H$_3$STe] was characterized by IR spectroscopy, elemental analysis[13] and

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