crystalline state, was, nonetheless, satisfying. In addition to **11a** small quantities of two other tetramethyl dilactones, **11b** (mp 115-116 °C)[6b] and **11c** (mp 124-129 °C),[6b] are observed in the bis-methylation reaction. The isomer ratio as well as reaction rate is temperature dependent—**11a**:**11b**:**11c**, temperature (time to achieve >90% bis-methylation): 58:10:1, -40 °C (4 h); 73:10:1, -78 °C (16 h); 9:1:trace, ~-110 °C (90 h).

The acid stability of **8a** and **11a** is exemplified by their inertness to AcOH-H_2O-THF (1:1:15) at room temperature. Use of trifluoroacetic acid in lieu of AcOH resulted in a smooth opening to racemic keto diacids *d,l*-**5** and **1** [99% (>95% pure), mp 125-126 °C][6a] without epimerization. Diazomethane converted **1** to **12**.[6a,18] Exploitation of the structural relationship between **1** and the venturicidin aglycon (**2**) via this stereoselective, five-step, premeditated synthesis of **1** is under way.

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Supplementary Material Available: Lists of final atomic positional parameters, atomic thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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[18] No evidence for pseudoester formation was observed in CH_2N_2 mediated conversions of **1** → **12** or **4** and **5** to their dimethyl esters.

Synthesis and Characterization of a Cyclic Bimetallic Complex of the Trisulfide Ion

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We wish to report the synthesis and characterization of a new inorganic ring system and the first example of a metal complex of the S_3 moiety. These results bear on the rapidly expanding field of the coordination chemistry of sulfur rich metal complexes, previous studies having identified examples of S_2,[1] S_4,[2] and S_5[2-4] fragments functioning as ligands. Such compounds are of potential relevance to sulfur transfer catalysis by metal ions in biology[4,5] and industry.[6,7]

Treatment of $(\eta^5\text{-}C_5H_5)_2TiS_5$[8] (**1**) with PPh_3 (2 equiv) in refluxing dichloromethane resulted in a rapid color change from red to black. Extraction of the resultant microcrystalline precipitate with dichloromethane gave an intensely blue solution which afforded black crystals from toluene (38% yield). Analytical and ^1H NMR data were consistent with a diamagnetic compound of the formula $(\eta^5\text{-}C_5H_5)_2Ti^{IV}S_3$ which contained equivalent cyclopentadienyl rings.[9] Field desorption mass spectrometry indicated that this new compound was a dimer, $(C_5H_5)_4Ti_2S_6$ (**2**), a result confirmed by an X-ray crystallographic analysis of the analogous $[(\eta^5\text{-}C_5H_4CH_3)_2TiS_3]_2$.[10]

Table I. Important Metrical Parameters for $(CH_3C_5H_4)_4Ti_2S_6$

	Bond Distances (Å)		
Ti(1)-S(1)	2.416 (1)	S(2)-S(3)	2.054 (1)
Ti(1)-S(4)	2.434 (1)	Ti(1)-CpA	2.067 (4)
S(1)-S(2)	2.058 (1)	Ti(1)-CpB	2.059 (4)
	Bond Angles (Deg)		
S(1)-Ti(1)-S(4)	96.08 (3)	S(5)-S(4)-Ti(1)	113.97 (4)
S(2)-S(1)-Ti(1)	116.93 (5)	CpA-Ti(1)-CpB	132.6 (2)
S(3)-S(2)-S(1)	109.07 (6)		
	Dihedral Angles (Deg)		
Ti(1)-S(1)-S(2)-S(3)	62.7	S(1)-Ti(1)-S(4)-S(5)	59.1
Ti(1)-S(4)-S(5)-S(6)	66.6	S(2)-S(1)-Ti(1)-S(4)	68.6

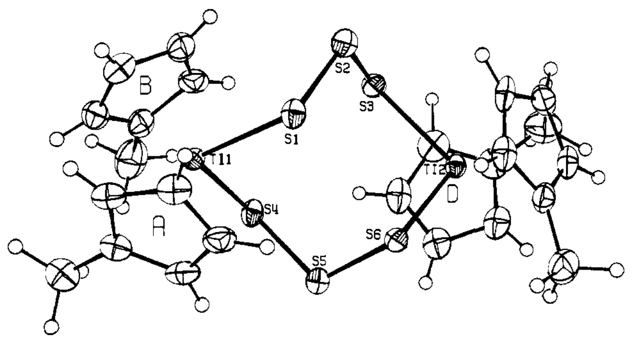

Figure 1. ORTEP plot of the $(CH_3C_5H_4)_4Ti_2S_6$ molecule with thermal ellipsoids drawn at the 50% prabability level.

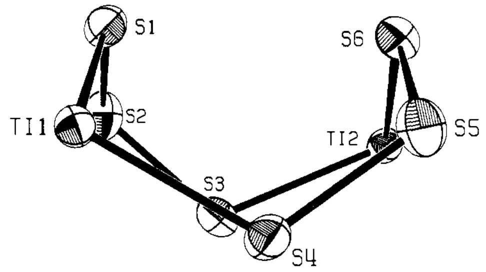

Figure 2. ORTEP plot of the Ti_2S_6 ring atoms of the $(CH_3C_5H_4)_4Ti_2S_6$ molecule.

A 0.24 × 0.58 × 0.58 mm crystal obtained by slow diffusion of C_6H_{14} into a CH_2Cl_2 solution of **2** at -20 °C was used for data collection. The space group and cell data are as follows: monoclinic, space group $P2_1/c$ with $a = 12.559$ (2) Å, $b = 15.054$ (3) Å, $c = 14.211$ (2) Å, $\beta = 99.24$ (1)°, $V = 2652.0$ (7) Å^3, $d(\text{calcd}) = 1.514$ g cm^{-3}, $d(\text{found}) = 1.49$ g cm^{-3}, and $Z = 4$. Three-dimensional diffraction data (a total of 6130 independent reflections having $2\theta(\text{Mo } K\bar{\alpha}) \leq 55.0°$) were collected on a Syntex $P2_1$ autodiffractometer, using graphite-monochromated Mo $K\bar{\alpha}$ radiation. The titanium atoms and four of the six sulfur atoms were located by direct methods.[11,12] Subsequent difference Fourier maps revealed the positions of all remaining atoms. Least-squares refinement to convergence using anisotropic thermal parameters

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[9] Anal. Calcd for $C_{10}H_{10}S_3Ti$: C, 43.79; H, 3.68; S, 35.07; Ti, 17.46. Found: C, 43.50; H, 3.71; S, 34.08; Ti, 17.17. ^1H NMR (CS_2, 220 MHz): at 15 °C, δ 6.03 (s, C_5H_5), at -50 °C, δ 6.01. Field desorption mass spectrum: *m/e* 548 (M^+). IR (mineral oil mull): 1070, 1026, 1013, 818, 380, 275 cm^{-1}.

[10] $[(CH_3C_5H_4)_2TiS_3]_2$ is made in an analogous manner to that for the C_5H_5 analogue. This derivative is easily obtained as X-ray quality single crystals; however, due to its solubility characteristics it is more difficult to separate from the Ph_3PS than the C_5H_5 derivative.

[11] A full discussion of the X-ray analysis and refinement will be described in a full paper.

[12] Sheldrick, G. M. SHELX 76, University of Cambridge, England, 1976.

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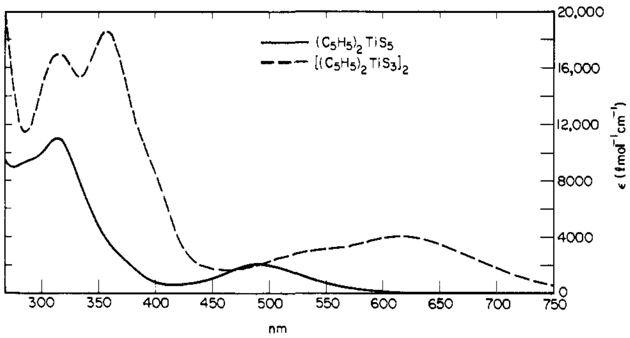
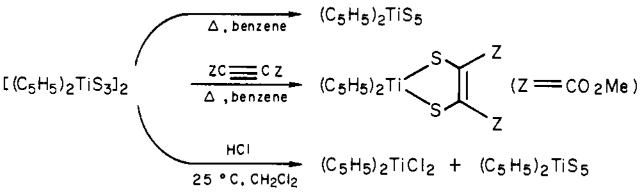


Figure 3. Electronic absorption spectrum of $(C_5H_5)_4Ti_2S_6$ and $(C_5H_5)_2TiS_5$ in CH_2Cl_2.

Scheme I



for all nonhydrogen atoms gave $R = 0.036$ and $R_w = 0.043$.[13]

The structure of **2** (Figure 1) consists of an eight-membered ring of approximate D_2 symmetry and contains alternating $(\eta^5\text{-}C_5H_4CH_3)_2Ti$ and S_3 fragments. Unlike cyclo-S_8,[14] **2** adopts a cradle conformation (Figure 2) wherein the titanium atoms are positioned at sites adjacent to the apical sulfurs. There is some asymmetry in the way that each S_3 unit interacts with a given titanium atom as manifested not only in the TiS distances but also in the Ti-S-S-S and STiSS dihedral angles (62.8° (average) vs. 66.8° (average) and 69.0° (average) vs. 58.9° (average), respectively). The coordination sphere about the titanium atoms resembles that observed for Cp_2TiS_5.[15,16] The XMX angle of Cp_2MX_2 complexes is known to be sensitive to the occupancy of the metal-based a_{1g} orbital;[16] the observed STiS angle is inconsistent with the titanium(III) formulation (suggested by its blue color) where an angle of ca. 89° would be expected (cf. $(C_5H_5)_2VS_5$).[15] While the S-S bond distances are completely normal for single bonds, the S-S-S angles are expanded and the dihedral angles are compressed relative to known cyclic polysulfides.[14]

One unique feature associated with **2** is its blue color which results from a low-energy absorption band centered at 610 nm (Figure 3). Such an absorption maximum is unusual for bis(cyclopentadienyl)titanium(IV) complexes but is reminiscent of that for S_8^{2+} ($\lambda_{max} = 590$ nm, $\epsilon = 2500$ L mol^{-1} cm^{-1}).[17,1,] The proposed titanium(IV) oxidation state requires the S_3^{2-} formulation while the long transannular S···S bond distances.[19] militate against strong S···S interactions of the type recognized for S_8^{2+},[20] S_4N_4, and other electron-deficient sulfur rings.[21,22]

We have surveyed the reactivity of **2** and some of the salient results are indicated in Scheme I. Heating **2** in benzene solution promotes the formation of the red pentasulfide, **1**, together with some insoluble, presumably polymeric residue. **2** shows enhanced reactivity relative to **1** toward dimethylacetylenedicarboxylate, affording the dithiolene.[23] Surprisingly, protonolysis of **2** with anhydrous HCl does not lead to scission of all titanium sulfur bonds but instead affords an apparently equimolar mixture of $(C_5H_5)_2TiCl_2$ and **1**. A likely mechanism for this process involves the formation of an intermediate containing an $\eta^1\text{-}S_3H$ moiety followed by cyclization with concomitant elimination of $(C_5H_5)_2Ti(SH)Cl$.

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(13) The function minimized was $\sum w||F_o| - |F_c||^2$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, and $R_w = [\sum w||F_o| - |F_c||^2/\sum_w|F_o|^2]^{1/2}$.

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(19) S(1)···S(3) = 3.349 (1) Å; S(1)···S(4) = 3.606 (1) Å; S(1)···S(6) = 3.529 (1)Å.

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(22) For a general review, see ref 18.

(23) The conversion of $(C_5H_5)_2TiS_5$ to the dithiolene by reaction with dimethylacetylenedicarboxylate requires more vigourous conditions than those for $(C_5H_5)_5Ti_2S_6$: Bolinger, C. M; Rauchfuss, T. B., to be published. This dithiolene has been subsequently characterized crystallographically.

(24) Subsequent to submission of this article we have prepared and characterized the *red* complex, $(CH_3C_5H_4)_4Ti_2S_4$: Bolinger, C. M., Rauchfuss, T. B. to be submitted for publication.

Synthesis of the Left-Hand Segment of the Antitumor Agent CC-1065

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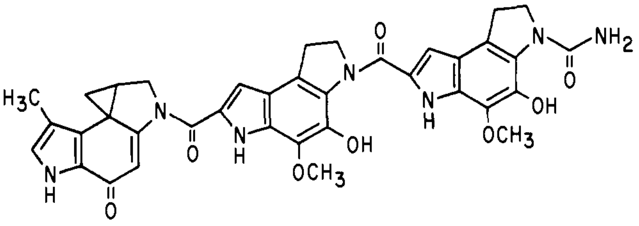
Recently a highly cytotoxic agent, CC-1065, was isolated from *Streptomyces zelensis*[1] and shown to have novel structure **1**.[2] This substance exhibited notable potency against L1210 in vitro and against the L1210 and P388 leukemias in mice as well as B16 melanoma,[3] proving to be the most cytotoxic antitumor agent known. Preferential binding of CC-1065 in the minor groove of double-stranded DNA at AT-rich regions in a nonintercalative fashion has been demonstrated.[4] Cursory examination of the structure of CC-1065 suggested that the unique left-hand segment[5] incorporates a potential "alkylating" capability to the structure. This capability might be a partial mechanism of action. To isolate



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(5) The identical middle and right-hand segments, 1,2-dihydro-3*H*-pyrrol[3,2-*c*]indoles, are the same as the 3′,5′-AMP phosphodiesterase inhibitor, PDE-I, isolated by: Enomoto, Y.; Furutani, Y.; Naganawa, H.; Hamada, M.; Takeuchi, T.; Umezawa, H. *Agric. Biol. Chem.* **1978**, *42*, 1331-1336. A 12-step synthesis of this ring system was reported by the same group: Komoto, N.; Enomoto, Y.; Miyagaki, N.; Tanaka, Y.; Nitanai, K.; Umezawa, H. *Ibid.* **1979**, *43*, 557-559.

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