(w), 731 (ms), 714 (m), 599 (m), 570 (w), 548 (w), 535 (vw), 475 (m), 405 (w) cm^{-1}. The mass spectrum contained peaks at 889 (M – OC(CF$_3$)$_3$)$^+$, 419 (M – (OC(CF$_3$)$_3$)$_3$)$^+$, 197 ((CF$_3$)$_3$CO – 2F)$^+$, 184 S$_4$N$_4$$^+$, 147 ((CF$_3$)$_2$CO – F)$^+$, 138 S$_3N_3$$^+$, 128 ((CF$_3$)$_2$CO – 2F)$^+$, 97 (CF$_3$CO)$^+$, 92 S$_2N_2$$^+$, 69 CF$_3$$^+$, 46 SN$^+$.

Anal. Calcd for $C_{16}F_{36}N_4S_4O_4$: C, 17.09; N, 4.98; S, 11.41; F, 60.8. Found: C, 17.21; N, 5.17; S, 10.78; F, 62.3.

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Structure of *trans*-Bis(1,5-dithiacyclooctane)tetrachlorotin(IV): Evidence for an Intramolecular Interaction between a Remote Donor and a Coordinated Atom

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The observation of an intramolecular interaction between a remote electron-pair donor and a coordinated atom was recently reported by Stein and Taube in ruthenium complexes containing a monodentate 1,5-dithiacyclooctane (1,5-DTCO) ligand [(NH$_3$)$_5$Ru(1,5-DTCO)]$^{2+,3+}$.[1] The spectroscopic properties of the ruthenium(III) complex and the redox characteristics of the ruthenium(II) complex both reflected an involvement of the remote thioether group. Unfortunately, no crystals of these complexes could be obtained, and no other crystal studies of a complex having monodentate coordination of a normally bidentate ligand in which the remote donor could interact with the coordinated donor have been reported. In the course of our studies of the coordination properties of mesocyclic dithioethers, we isolated and determined the crystal structure of *trans*-SnCl$_4$(1,5-DTCO)$_2$. A relatively short nonbonded contact of 3.271 (3) Å between the two sulfur atoms was found. Since a similar interaction may be responsible for the unusual properties of the monodentate ruthenium complexes of 1,5-DTCO, we are reporting the structure of the tin(IV) complex at this time. The complex was prepared by combining equal volumes of about 5% solutions of 1,5-DTCO[2] and SnCl$_4$ in acetonitrile in a dry tube. The tube was lightly stoppered and set aside for several weeks at ambient temperature. The crystals deposited on the sides of the tube; far IR 367 (m) 312 (vs), 277 (m) cm^{-1}.

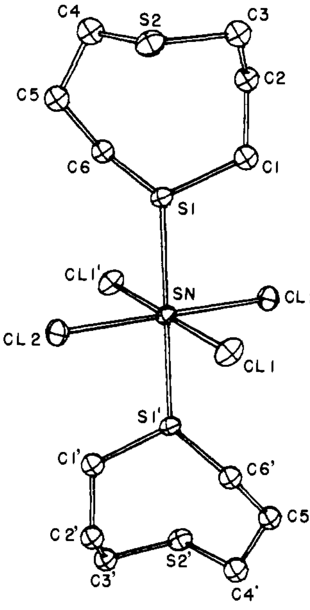

Figure 1. Perspective drawing of *trans*-SnCl$_4$(1,5-DTCO)$_2$ showing the atom numbering scheme.

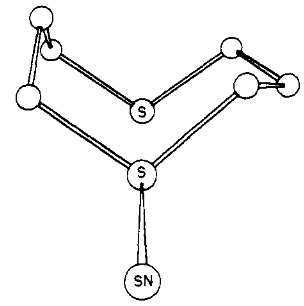

Figure 2. Drawing of one of the coordinated 1,5-DTCO rings showing the boat–chair conformation.

Table I. Bond Distances (Å) and Bond Angles (Deg) for *trans*-SnCl$_4$(1,5-DTCO)$_2$

Sn-Cl(1)	2.414 (1)	Cl(1)-Sn-Cl(2)	89.8 (1)
Sn-Cl(2)	2.428 (1)	Cl(1)-Sn-S(1)	84.1 (1)
Sn-S(1)	2.602 (1)	Cl(2)-Sn-S(1)	83.1 (1)
S(1)-C(1)	1.827 (3)	Sn-S(1)-C(1)	106.6 (1)
S(1)-C(6)	1.828 (3)	Sn-S(1)-C(6)	105.0 (1)
S(2)-C(2)	1.820 (3)	S(1)-C(1)-C(2)	115.7 (2)
S(2)-C(4)	1.821 (3)	S(1)-C(6)-C(5)	113.3 (2)
C(1)-C(2)	1.522 (4)	S(2)-C(3)-C(2)	115.7 (2)
C(2)-C(3)	1.526 (4)	S(2)-C(4)-C(5)	114.5 (2)
C(4)-C(5)	1.529 (4)	C(1)-S(1)-C(6)	105.3 (1)
C(5)-C(6)	1.533 (4)	C(1)-C(2)-C(3)	117.0 (2)
		C(3)-S(2)-C(4)	102.0 (1)
		C(4)-C(5)-C(6)	117.9 (2)

The bifunctional nature of the dithioether ligand naturally leads one to expect either a polymeric ligand-bridged structure, as in the glutaronitrile complex *cis*-SnCl$_4$[NC(CH$_2$)$_3$CN]$_2$[3] or *trans*-Ni(1,5-DTCO)Cl$_2$,[4] or a bidentate functionality, as in (Ph$_3$P)$_2$Pt(1,5-DTCO).[5] The discovery of a monodentate 1,5-DTCO in the tin complex was therefore somewhat of a surprise. The structure[6] of *trans*-SnCl$_4$(1,5-DTCO)$_2$ consists of isolated neutral molecules with no short intermolecular contacts. Two molecules are contained in the unit cell, and they are therefore

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[6] A pale yellow plate of SnCl$_4$(C$_6$S$_2$H$_{12}$)$_2$, M_r 557.08, was cut to dimensions 0.45 × 0.45 × 0.70 mm and mounted on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator. With Mo Kα radiation (λ 0.71069 Å) and with the crystal cooled to 140 K, crystal data are as follows: monoclinic, space group $P2_1/c$; a = 7.544 (2) Å, b = 13.401 (6) Å, c = 10.090 (2) Å; β = 99.55 (2)°; Z = 2; μ = 21.9 cm^{-1} (range of absorption correction factors 4.2–5.6). Data were collected to $2\theta_{max}$ of 50° with an ω scan technique. A total of 1753 unique data were collected of which 1607 had $I > 2.5\sigma(I)$. No absorption or extinction corrections were performed. Scattering factors and corrections for anomalous scattering were from Vol. IV of the International Tables. Computer programs were those of the SHELXTL, version 3, July 1981 package. The structure was solved by placing the tin atom at (0.0, 0.0, 0.0) and computing a Fourier map. With anisotropic thermal parameters for non-hydrogen atoms and with hydrogen atoms riding on the bonded carbon, R = 0.021, R_w = 0.027 in the final cycle of refinement (67 parameters). Atomic coordinates, thermal parameters, and structure factor tables are available as supplementary data.

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Table II. Comparison of S···S Distances, E–S···S Angle, and Ring Conformation in Derivatives of 1,5-Dithiacyclooctane

compound	S···S, Å	ring conformation	E–S···S, deg	ref
1-acetonyl-1-thionia-5-thiacyclooctane perchlorate	3.121 (5)	boat–chair	178.9 (5)	*a*
1-methyl-1-thionia-5-thiacyclooctane iodide	3.258 (7)	chair–chair	174.0 (1)	*b*
trans-$SnCl_4$(1,5-DTCO)$_2$	3.271 (3)	boat–chair	171.5 (1)	*c*
catena-Ni(1,5-DTCO)$_2$$Cl_2$	3.335 (3)	disordered: boat–chair/chair–chair	164.0 (1) 166.1 (1)	*d*
1,5-DTCO·2I_2 (two molecules in the asymmetric unit)	I: 3.443 (8)	I: chair–chair	I: 166.3 (5) 171.3 (5)	*e*
	II: 3.227 (8)	II: boat–chair	II: 173.3 (5) 177.2 (5)	
1,5-dithiacyclooctane-3,7-dione ethylenediketal	3.576 (1)	twist–chair		*f*

[a] Johnson, S. M.; Maier, C. A.; Paul, I. C. *J. Chem. Soc. B* 1970, 1603–1608. [b] Olmstead, M. M., unpublished results. $S_2C_7H_{15}{}^+I^-$ crystallizes in the orthohombic space group $P2_1 2_1 2_1$ with a = 6.736 (3) Å, b = 12.287 (5) Å, c = 13.046 (4) Å. R = 0.030 for 46 least-squares parameters and 1438 unique observed reflections. Full details of this structure to be published. [c] This work. [d] Hill, N. L.; Hope, H. *Inorg. Chem.* 1974, *13*, 2079–2082. [e] Nichols, B. G. Ph.D. Dissertation, University of California, Davis, A, 1981. [f] Olmstead, M. M.; Musker, W. K. *Acta Crystallogr., Sect. B* 1981, *B37*, 261–263.

required to possess a center of symmetry. The coordination about tin is pseudooctahedral, with the four chlorine atoms in a square plane and two monodentate dithioether ligands above and below this plane (Figure 1). An angle of 9.1° is formed between the normal to the $SnCl_4$ plane and the SnS line. The conformation of the eight-membered dithioether ring is boat–chair (Figure 2). There is a transannular contact of 3.271 (3) Å between the two sulfur atoms. The important bond distances and angles are given in Table I. A comparison of the S···S distance to those found in other derivatives of 1,5-dithiacyclooctane is given in Table II.

The photoelectron spectrum of free 1,5-DTCO[7] shows a large splitting of the sulfur–sulfur lone-pair orbitals of 0.43 eV. This observation suggests that the two sulfur lone-pair orbitals must point toward each other to achieve such a large amount of mixing in the gas phase. On the basis of the photoelectron spectrum of 1,5-DTCO and molecular mechanics calculations, the boat–chair conformation has been predicted to be its most stable conformation.[7] Although the crystal structure determination of 1,5-DTCO itself has not been carried out, it can be seen from the compounds listed in Table II that the boat–chair conformation is the most common, and the chair–chair conformation is probably very similar to it in energy. In all of the boat–chair and chair–chair structures, the two sulfur atoms occupy identical 1,5-positions with respect to the ring conformation. In these positions the overlap between sulfur lone-pair orbitals is greater than it would be in the other possible transannular arrangements, in agreement with the large degree of mixing that is indicated by the photoelectron spectrum of 1,5-DTCO itself. It is tempting to conclude that, as positive charge is induced on the sulfur bound to tin, the interaction to the remote sulfur is strengthened. This effect is also thought to be operative in the anchimerically assisted iodine oxidation of thioethers, in which iodine bonds to a thioether sulfur and imparts to it a partial positive charge. The positively charged sulfur atom can then act as an electrophile toward the remote donors OH, NH_2, NHR, or R_2S.[8]

Additional evidence for a long-range intramolecular interaction is found in the angles E–S···S, where E is a substituent on sulfur. As can be seen from the angles tabulated in Table II, the shorter the S···S distance, the closer the E–S···S angle is to 180°. It is possible that theoretical calculations would show that this trend results from the presence of extended σ molecular orbitals over the systems I–I–S···S–I–I, S···S–Sn–S···S, (–Ni–S···S–Ni–S···S–), as well as three-center four-electron bonds in the R–S$^+$···S compounds.

Ligands having nitrogen or oxygen donors do not have the nominal capacity for accommodating more than eight electrons and therefore will be unable to function as mediators between a remote donor and a metal atom. Thus, only elements of the second row and higher can be expected to fulfill this role.

It has been proposed that in proteins a methionine sulfur can serve as mediator of electron transfer between a metal atom and remote electron pairs.[9] This structural evidence shows that such mediation may be present in the ground state of the molecule.

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Registry No. *trans*-$SnCl_4$(1,5-DTCO)$_2$, 82917-92-8.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and a listing of structure factor amplitudes for *trans*-$SnCl_4(C_6S_2H_{12})_2$ (13 pages). Ordering information is given on any current masthead page.

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Total Synthesis of Hibiscone C (Gmelofuran)

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Since the classic work by Eaton,[2] Corey,[3] and de Mayo,[4] the photochemical [2 + 2] cycloaddition of α,β-unsaturated carbonyl compounds to olefins has evolved as a significant and powerful synthetic tool for construction of a carbon framework.[5] In recent years the intramolecular version of this reaction has seen increasing popularity in natural product synthesis.[6] Surprisingly, however, a search of the literature revealed *no examples* of the intramolecular [2 + 2] photocycloaddition of enones to acetylenic moieties. In this communication we disclose the *first examples* of such a process as well as exploitation of this methodology as cornerstone for the *first* total synthesis of hibiscone C (gmelofuran), **1** (eq 1), a structurally novel furanosesquiterpenoid isolated from the

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