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Communication

A complex with the *cyclo*-$R_2Sb_2S_2$ [R = $CH(SiMe_3)_2$] ligand[†]

Hans Joachim Breunig*, Ioan Ghesner and Enno Lork

Institut für Anorganische und Physikalische Chemie, Fachbereich 2 der Universität Bremen, D-28334 Bremen, Germany

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The reaction of the *cyclo* oligomers $R_nSb_nS_n$ [n = 2, 3; R = $CH(SiMe_3)_2$] with $W(CO)_5thf$ (thf = tetrahydrofuran) in thf results in trapping of the dimer in *cyclo*-$[R_2Sb_2S_2][W(CO)_5]_2$ (1). An X-ray crystal structure analysis revealed that the complex contains a four-membered antimony–sulfur ring in an almost planar conformation, where the alkyl groups occupy *cis* positions and the $W(CO)_5$ units are bonded *trans* to the alkyl groups on the antimony atoms. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: antimony–sulfur ring; tungsten complex; X-ray structure

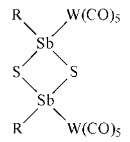
INTRODUCTION

Organoantimony sulfides *cyclo*-$R_nSb_nS_n$ [R = alkyl, aryl] have been under investigation since the end of the 19th century,[1,2] but little is known of the structural chemistry of these polymeric or cyclic compounds. In our previous work on *cyclo*-$R_nSb_nS_n$ [n = 2–4; R = $CH(SiMe_3)_2$], an NMR study revealed the presence of ring–ring equilibria between dimers and trimers in chloroform solution. In the gas phase, tetramers were also detected by mass spectrometry.[3] We report here on the trapping of the dimer, *cyclo*-$R_2Sb_2S_2$, as ligand in the binuclear complex *cyclo*-$[R_2Sb_2S_2][W(CO)_5]_2$ (**1**). Complexes with *cyclo*-$R_nSb_nS_n$ ligands have not been described before. Closely related compounds are *cyclo*-$R_2Sb_2O_2$,[4] *cyclo*-$R_2Sb_2S_4$,[5] RSbS,[6] *cyclo*-$RSbS_n$ (n = 1, 5, 7)[6] [R = 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$], and complexes with *cyclo*-$Ph_2P_2S_2$ ligands[7] or *cyclo*-$R_2E_2Se_2$ [R = ^{t}Bu, E = As; R = Ph, E = P] ligands.[8] Complexes derived from linear Sb—S ligands with known crystal structure are $[(Ph_2Sb{-}SPh)_3Mo(CO)_3]$,[9] $[(Ph_2Sb{-}S{-}SbPh_2)Cr(CO)_5]$,[10] *cyclo*-$[(Me_2Sb{-}S{-}SbMe_2)Cr(CO)_4]_2$, and *cyclo*-$[(Me_2Sb{-}S{-}SbMe{-}S{-}SbMe_2)Cr(CO)_4]\cdot[nbdCr(CO)_4]$ (nbd = norbornadiene).[11]

RESULTS AND DISCUSSION

The ring–ring equilibrium mixture of *cyclo*-$R_nSb_nS_n$ [n = 2, 3; R = $CH(SiMe_3)_2$] reacts with $W(CO)_5thf$ (thf = tetrahydrofuran) to form *cyclo*-$[R_2Sb_2S_2][W(CO)_5]_2$ (**1**) almost quantitatively:

$$\frac{2}{n}\text{cyclo-}R_nSb_nS_n + 2W(CO)_5\text{thf} \xrightarrow[-2\text{thf}]{25^\circ C} \qquad (1)$$
$$n = 2,3$$
$$R = CH(SiMe_3)_2$$



Brown crystals of **1** were obtained in a 68% yield by cooling petroleum ether solutions to −28 °C. **1** is slightly soluble in aromatic or aliphatic hydrocarbons and forms brown solutions in thf, dichloromethane, or chloroform. For a short time the complex is stable in air. Solutions of **1** under an argon atmosphere are stable for several days at room temperature. The highly selective formation of **1** is remarkable in view of the complexity of the initial mixture. The coordination of two $W(CO)_5$ units to the *cyclo*-$R_nSb_nS_n$ ligand increases the steric protection at the periphery of the antimony–sulfur ring, and under these conditions the dimeric form is favoured. We found no indication for the formation of a complex derived from coordination of the trimer *cyclo*-$R_3Sb_3S_3$ which was present in the initial mixture. Apparently, the trimer was transformed into the dimer on complexation.

The structure of **1** was determined by single crystal X-ray diffractometry (see Table 1 for details). The molecular structure is shown in Fig. 1. It consists of an almost planar

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*Correspondence to: H. J. Breunig, Institut für Anorganische und Physikalische Chemie, Fachbereich 2 der Universität Bremen, D-28334 Bremen, Germany.

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Table 1. Crystal data, data collection, and structure refinement parameters for *cyclo*-$[R_2Sb_2S_2][W(CO)_5]_2$ [R = $CH(SiMe_3)_2$] (**1**)

Empirical formula	$C_{24}H_{38}O_{10}S_2Sb_2Si_4W_2$
Formula weight	1274.22
Colour	yellow
Temperature (K)	173(2)
Crystal size (mm^3)	0.6 × 0.4 × 0.4
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	22.396(5)
b (Å)	10.919(4)
c (Å)	17.183(4)
α (deg)	90
β (deg)	98.08(2)
γ (deg)	90
Volume (Å^3)	4160(2)
Z	4
Density (calc.) (Mg m^{-3})	2.034
μ(Mo Kα) (mm^{-1})	7.054
Scan method	ω–2θ
F(000)	2400
θ range for data collection (deg)	$2.81 \leq \theta \leq 27.51$
Completeness to $\theta = 27.51°$ (%)	99.4
No. of measured data	10 582
No. of unique data	4757 ($R_{int} = 0.0316$)
No. of parameters	207
Absorption correction	DIFABS[12]
wR_2[a] (all data)	0.0632
R_1[a] (all data)	0.0288
wR_2[a] ($I > 2\sigma(I)$)	0.0621
R_1[a] ($I > 2\sigma(I)$)	0.0258
Goodness-of-fit on F^2	1.133
Residual density (e$^-$ Å^{-3})	+1.160; −1.282

[a] Definition of the R values: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{[w\sum(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (\alpha P)^2 + bP$.

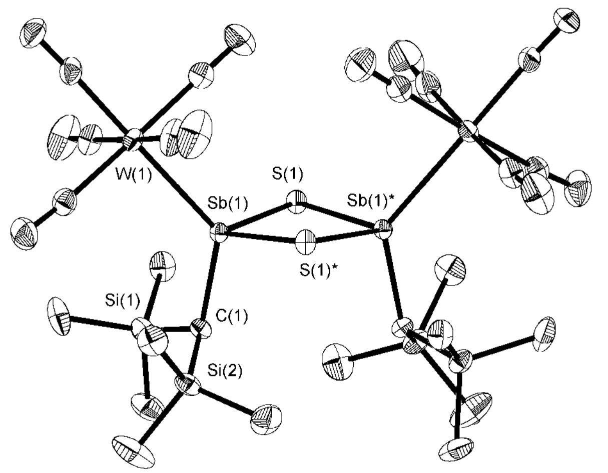

Figure 1. ORTEP representation of the structure of *cyclo*-$[R_2Sb_2S_2][W(CO)_5]_2$ [R = $CH(SiMe_3)_2$] (**1**). Thermal ellipsoids are represented with 50% probability. Selected bond lengths (Å) and angles (°) are as follows: Sb(1)—S(1), 2.425(1); Sb(1)—S(1)*, 2.428(1); Sb(1)—C(1), 2.143(4); W(1)—Sb(1), 2.737(7); Sb(1)···Sb(1)*, 3.423(3); S(1)···S(1)*, 3.420(2); W(1)—C_{ax}, 1.996(4); W(1)—C_{eq}, 2.032(4)–2.048(5); Sb(1)—S(1)—Sb(1)*, 89.67(3); S(1)—Sb(1)—S(1)*, 89.61(3); C(1)—Sb(1)—S(1), 103.8(1); C(1)—Sb(1)—S(1)*, 99.9(1); C(1)—Sb(1)—W(1), 128.61(10); S(1)—Sb(1)—W(1), 112.24(3); S(1)*—Sb(1)—W(1), 115.28(3).

four-membered Sb_2S_2 ring (mean deviation from plane 0.0965 Å) with alternating antimony and sulfur atoms. The dihedral angles between the Sb—S—S or S—Sb—Sb planes are 12.9°. In *cyclo*-$R_2Sb_2O_2$ [R = 2,4,6–$[(Me_3Si)_2CH]_3C_6H_2$], which crystallizes as a *trans* isomer, no deviation from the planarity was observed.[4] In **1**, both antimony atoms of the ring are coordinated to $W(CO)_5$ units, which occupy *cis* positions relative to the ring and *trans* positions relative to the alkyl groups. The Sb—S bond lengths [2.425(1) and 2.428(1) Å] in **1** are similar to those found in other known complexes with Sb—S ligands (e.g. *cyclo*-[(Me_2Sb—S—SbMe—S—$SbMe_2$)$Cr(CO)_4$]·[nbd$Cr(CO)_4$], 2.433(9) and 2.412(8) Å; *cyclo*-[(Me_2Sb—S—$SbMe_2$)$Cr(CO)_4$]$_2$, 2.424(9) and 2.421(5) Å),[11] but are shorter than in the case of the solid Me_2Sb—S—$SbMe_2$ [2.498(1) Å].[13] The endocyclic angles on the antimony and sulfur atoms are both close to 90°, with Sb(1)—S(1)—Sb(1)* = 89.67(3)° and S(1)—Sb(1)—S(1) = 89.61(3)°, and describe an almost ideal square. The Sb—W bond lengths [2.737(7) Å] correspond to the sum of the van der Waals radii for antimony and tungsten (2.78 Å) and are similar to the values found in *cyclo*-[$Cr(CO)_4$(Me_2Sb—SbR—SbR—$SbMe_2$)$W(CO)_5$] [R = Me_3SiCH_2, Sb—W = 2.791(6) Å].[14] Longer Sb—W bonds were found in *cyclo*-$[^tBu_4Sb_4][W(CO)_5]_2$ [2.847(3) and 2.822(2) Å].[15] The Me_3Si groups of the *cis* alkyl substituents are directed outwards, and together with the $W(CO)_5$ groups they shield the molecules from each other. Consequently, close intermolecular contacts are not observed in the crystals of **1**. A similar *cis* orientation of the $CH(SiMe_3)_2$ groups also exists in *cyclo*-R_3Sb_3 [R = $CH(SiMe_3)_2$].[16] The formation of **1** in the *cis* form does not necessarily also prove a *cis* preference for the free ligand *cyclo*-$R_2Sb_2S_2$, which contrasts with the *trans* orientation of the organic groups in crystals of *cyclo*-$R_2Sb_2O_2$ [R = 2, 4, 6–$[(Me_3Si)_2CH]_3C_6H_2$].[4]

1 was also characterized by IR, ^1H and ^{13}C NMR and by mass spectrometry using desorptive chemical ionization DCI techniques. The NMR spectra of **1** in C_6D_6 are consistent with the structure established by X-ray diffraction and contain the expected singlet signals for equivalent Me_3Si or CH groups. However, the same pattern of the spectra is also to be expected for the *trans* isomer. The ring-ring equilibria observed for the free *cyclo*-$R_nSb_nS_n$ ligand are not retained after complexation. The DCI mass spectra contain molecular ions at highest mass. Fragmentation occurs mainly by loss of the groups bonded to the antimony atom. The IR spectra of **1** show the common pattern for complexes of the type $LW(CO)_5$. The composition of **1** has been proven by elemental analyses.

EXPERIMENTAL

General comments

NMR spectra were run on a Bruker DPX 200 spectrometer. Chemical shifts are reported in δ units (ppm) referenced to C_6D_5H (7.15 ppm, ^1H) and C_6D_6 (128.0 ppm, ^{13}C). Mass spectra were recorded on a Finnigan MAT CH7 (A) spectrometer. The pattern of antimony-containing ions was compared with theoretical values. For the IR spectra, an FT-IR SPEKTRUM 1000 instrument was used. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller in Göttingen. The reactions and manipulations were performed in an atmosphere of dry argon. *cyclo*-$R_nSb_nS_n$ [$n = 2{,}3$; $R = CH(SiMe_3)_2$] was prepared according to a reported procedure.[3]

cyclo-$[R_2Sb_2S_2][W(CO)_5]_2$ [$R = CH(SiMe_3)_2$] (1)

0.28 g (0.44 mmol) of *cyclo*-$R_nSb_nS_n$ and $W(CO)_5$thf prepared from 0.31 g (0.88 mmol) $W(CO)_6$ by irradiation with a UV lamp, in 150 ml of thf were stirred for 5 h at room temperature. Thereafter, the solvent was removed under reduced pressure and the remaining brown product was washed twice with 50 ml of petroleum ether. 0.38 g (68 %) of brown crystals [m.p. 152 °C (dec.)] were obtained by cooling at −28 °C petroleum ether solutions of **1**. Anal. Found: C, 22.77; H, 2.99. Calc. for $C_{24}H_{38}O_{10}S_2Sb_2Si_4W_2$ (1274.22): C, 22.62; H, 3.01 %. ^1H NMR (C_6D_6, 200 MHz): 0.22 (s, 18 H, $(CH_3)_3Si$, $^1J_{CH} = 119.2$ Hz, $^2J_{SiH} = 6.3$ Hz), 0.38 (s, 1 H, CH). ^{13}C NMR (C_6D_6, 50 MHz): 2.94 (s, $(CH_3)_3Si$), 37.51 (s, CH), 196.01 (s, CO_{eq}), 197.69 (s, CO_{ax}). MS (DCI_{pos}, NH_3) *m/z* (%): 1291 (18) $[M^+ + NH_4]$, 1274 (13) $[M^+]$, 952 (19) $[M^+ - W(CO)_5]$, 887 (24) $[R_2Sb_2W(CO)_5^+]$. MS (DCI_{neg}, NH_3) *m/z* (%): 1115 (22) $[M^- - R]$, 950 (30) $[M^- - W(CO)_5]$, 866 (14) $[M^- - W(CO)_5, -3\ CO]$, 791 (46) $[M^- - W(CO)_5, -R]$, 680 (56) $[M^- - W(CO)_5, -4\ CO, -R]$, 638 (28) $[[RSbS][W(CO)_5]^-]$, 594 (32) $[R_2Sb_2S^-]$, 582 (30) $[[RSbS][W(CO)_3]^-]$, 324 (78) $[W(CO)_5^-]$, $R = CH(SiMe_3)_2$. IR (toluene; cm^{-1}): 2081 vs, 2074s, 1919m (νCO).

Supplementary data

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK, and can be obtained from them.

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