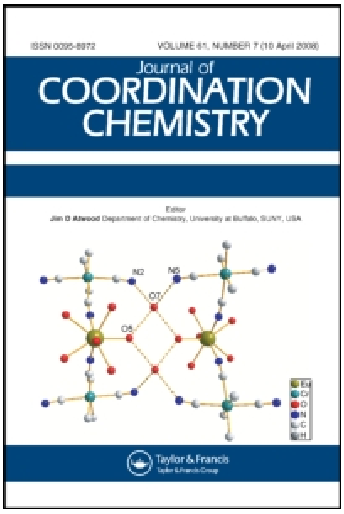

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The First Structurally Characterized Trithionantimonite Transition Metal Complex, $(CO)_5W(\mu\text{-}SBu^t)Sb(SBu^t)_2$, Exhibiting a Novel Mode of Coordination for the Trithioantimonite Ligand $Sb(t\text{-}BuS)_3$

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THE FIRST STRUCTURALLY CHARACTERIZED TRITHIONANTIMONITE TRANSITION METAL COMPLEX, $(CO)_5W(\mu\text{-}SBu^t)Sb(SBu^t)_2$, EXHIBITING A NOVEL MODE OF COORDINATION FOR THE TRITHIOANTIMONITE LIGAND $Sb(t\text{-}BuS)_3$

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Reaction of $Sb(SBu^t)_3$ with $W(CO)_6$ in THF gives $(CO)_5W(\mu\text{-}SBu^t)Sb(SBu^t)_2$, (1). The structure of (1) was been determined by single crystal X-ray diffraction methods. Crystal data for (1): $C_{17}H_{27}O_5S_3SbW$, M = 713.2, monoclinic, space group $P2_1/n$ (No. 1014), a = 9.892 (2), b = 17.489 (4), c = 15.014 (3) A, Z = 4, U = 2597.1 (5) Å^3, D_c = 1.824 g cm^{-3}, $\lambda(\text{Mo}K_\alpha)$ = 0.71073 Å, graphite monochromator, μ = 58.22 cm^{-1}. Methods: Multan, difference Fourier, full-matrix least-squares. Refinement of 3083 reflections ($I > 3\sigma(I)$) out of 4732 unique observed reflections ($2° < 2\theta < 50°$) gives current R and R_w values of 0.043 and 0.047, respectively. All nonhydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were not located. Data/parameter ratio = 12.6, shift to error ratio = 0.39, highest peak in final difference Fourier = 0.66 eÅ^{-3}. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 2°C. The $Sb(SBu^t)_3$ ligand binds to W *via* S giving the W atom an octahedral coordination geometry. Two of the angles subtended at Sb are ca. 90° and suggest little sp^3 hydrization for this atom.

Keywords: X-ray structure, tungsten, trithioantimonate, carbonyl, complex

INTRODUCTION

Trithioanimonates ($Sb(SR)_3$) have been known for nearly 40 years and have found applications in the treatment of protozoan diseases[1] and as catalysts for polyester synthesis[2]. It is, therefore, surprising that no structural information is available for this important class of molecules. In addition, very little is known of their reactions with transition metal complexes. Until this report, the only transition metal complex of a trithioanimonite known was $Pt(PPh_3)_2[Sb(SPh)_3]_2$ reported in 1976 by Garrou and Hartwell.[3] This is an insoluble yellow material characterized only by C and H microanalysis, and no information is available on the mode of bonding of the $Sb(SPh)_3$ units to Pt.

We report here the synthesis and X-ray crystal structure of $(CO)_5W(\mu\text{-}SBu^t)Sb(SBu^t)_2$, (**1**). Of key significance is the novel coordination mode adopted by the potentially ambidentate trithioantimonite ligand. This unit is bound to W *via* S and *not* Sb, probably reflecting the better donor ability of S *vs* Sb.

RESULTS AND DISCUSSION

Photolysis of a mixture of $W(CO)_6$ with $Sb(SBu^t)_3$[4] in THF under nitrogen yields a red-brown solution from which bright yellow crystals of (**1**) may be isolated in *c a* 57% yield.

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TABLE I
Crystal structure parameters for complex (**1**):

Description of crystal	
Colour	Yellow
Habit	Prism
Max. crystal dimension (mm)	0.25 × 0.15 × 0.10
Unit cell	
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell parameters:	
a(Å)	9.892(2)
b(Å)	17.489(4)
c(Å)	15.014(3)
α(deg)	90
β(deg)	91.00(2)
γ(deg)	90
U(Å^3)	2597.1 (4)
Molecules per unit cell	4
Formula	$C_{17}H_{27}O_5S_3SbW$
Molecular weight (g mol^{-1})	713.19
Calculated density (g cm^{-3})	1.824
μ-calc. (cm^{-1})	58.224
Data collection	
Radiation (Å)	MoK_α(0.71073)
Scan technique	$\omega/2\theta$
Scan width (deg)	0.8 + 0.35 (tan θ)
Range of indices	$\pm h$, $+k$, $+1$
2θ range (deg)	2.0 to 50.0
No. reflections measured	4918
Standard reflections:	
intensity	$\bar{5}\,\bar{3}\,1,\ 0\,\bar{8}\,\bar{5}$
orientation	$\bar{2}\,\bar{1}\,\bar{8},\ \bar{4}\,2\,\bar{5}$
Decay of standards	0.8%
Min. % transmission	52.09
Max. % transmission	99.86
Average % transmission	79.77
Agreement factor for averaged reflections: F (*obs*)	0.041
intensity	0.037
Structure determination	
No. reflections used ($I > 3\,\sigma\,(I)$)	3083
No. parameters varied	244
Data/parameter ratio	12.635
Shift to error ratio	0.391
E.s.d. of an observation of unit weight	5.17
R	0.043
R_w	0.047

(**1**) is air stable for short periods in the solid state and decomposes more rapidly in solution when exposed to the atmosphere. The ^{1}H NMR spectrum in C_6D_6 at ambient temperature is in accord with the solid state structure. Thus, two singlets of relative areas 1:2 are observed at δ 1.42 and 1.35.

(**1**) crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. Relevant crystal structure parameters are given in Table I and bond lengths and angles in Tables II and III. Positional parameters are in Table IV.

A view of the molecule is shown in Figure 1. The coordination geometry about W is essentially octahedral with C(4)-W(1)-S(1) = 173.1 (5)°. The trithioantimonate ligand is

TABLE II
Bond lengths for (**1**).

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
W1	S1	2.596(1)	O2	C2	1.152(7)
W1	C1	2.013(6)	O3	C3	1.120(7)
W1	C2	1.982(6)	O4	C4	1.111(7)
W1	C3	2.037(7)	O5	C5	1.121(6)
W1	C4	1.953(6)	C6	C7	1.502(9)
W1	C5	2.042(6)	C6	C8	1.57(1)
Sb	S1	2.492(1)	C6	C9	1.570(9)
Sb	S2	2.395(2)	C10	C11	1.52(1)
Sb	S3	2.397(2)	C10	C12	1.55(1)
S1	C6	1.887(5)	C10	C13	1.52(1)
S2	C10	1.843(6)	C14	C15	1.59(1)
S3	C14	1.869(6)	C14	C16	1.48(1)
O1	C1	1.145(7)	C14	C17	1.58(1)

Numbers in parentheses are estimated standard deviations.

TABLE III
Bond angles for (**1**)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S1	W1	C1	83.6(4)	W1	C3	O3	173.(2)
S1	W1	C2	94.4(5)	W1	C4	O4	178.(2)
S1	W1	C3	97.9(5)	W1	C5	O5	171.(1)
S1	W1	C4	173.1(5)	S1	C6	C7	110.(1)
S1	W1	C5	95.6(4)	S1	C6	C8	106.(1)
C1	W1	C2	177.9(6)	S1	C6	C9	103.(1)
C1	W1	C3	89.2(6)	C7	C6	C8	116.(2)
C1	W1	C4	89.8(6)	C7	C6	C9	112.(1)
C1	W1	C5	90.8(6)	C8	C6	C9	108.(1)
C2	W1	C3	90.4(7)	S2	C10	C11	110.(1)
C2	W1	C4	92.2(7)	S2	C10	C12	112.(1)
C2	W1	C5	90.2(6)	S2	C10	C13	107.(1)
C3	W1	C4	83.8(6)	C11	C10	C12	108.(2)
C3	W1	C5	166.4(6)	C11	C10	C13	112.(2)
C4	W1	C5	82.6(6)	C12	C10	C13	108.(2)
W1	S1	Sb	115.9(1)	S3	C14	C15	104.(1)
W1	S1	C6	117.8(5)	S3	C14	C16	110.(1)
Sb	S1	C6	106.0(5)	C15	C14	C16	114.2(2)
W1	C1	O1	178(1)	S1	Sb	S2	90.75(6)
W1	C2	O2	179.(2)	S1	Sb	S3	102.44(6)
				S2	Sb	S3	90.95(6)

Numbers in parentheses are estimated standard deviations.

bound to W *via* S(1) with W(1)-S(1) = 2.596(1) Å. This is similar to other W-S distances in $(CO)_5$ W-sulfur complexes where S behaves as a simple two-electron donor.[5]

The geometry about S(1) is also of interest. The Sb-S(1) distance is considerably longer than the other two Sb-S lengths (Sb-S(1) = 2.492(1) Å, Sb-S(2) = 2.395(2) Å, Sb-S(3) = 2.397(2) A). These distances can be compared to an Sb-S distance of 2.41 Å (av.) in $ClSbS_2(CH_2)_2$[6] and to Sb=S of 2.244(1) Å in $Ph_3Sb{=}S$.[7] In addition, the Sb-S(1)-C(6) angle of 106.0(5)° is close to an idealized tetrahedral value while the W(1)-S(1)-Sb and W(1)-S(1)-C(6) angles of 115.9(1)° and 117.8(5)° are considerably larger. This could be due to some degree of steric repulsion between the tungsten center and the Bu^t and Sb groups bonded to S(1).

TABLE IV
Positional parameters for (**1**)

Atom	x/a	y/b	z/c	$B(\AA^2)$
W1	0.11808(5)	0.09545(3)	0.76010(4)	3.599(9)
Sb	−0.31769(9)	0.08762(5)	0.75087(6)	4.17(2)
S1	−0.1030(4)	0.0223(2)	0.7953(2)	4.09(7)
S2	−0.2223(5)	−3149(2)	0.6398(3)	5.42(9)
S3	0.2536(5)	0.3285(2)	1.1345(3)	5.65(9)
O1	0.152(1)	0.0966(9)	0.9696(8)	8.7(4)
O2	0.077(2)	0.0868(8)	0.5529(7)	9.0(4)
O3	0.323(1)	−0.0422(7)	0.7521(9)	8.7(4)
−O4	0.378(1)	0.1889(9)	0.740(1)	10.4(4)
O5	0.002(1)	0.2635(6)	0.7622(8)	6.2(3)
C1	0.141(1)	0.0975(8)	0.8935(9)	4.9(3)
C2	0.090(2)	0.090(1)	0.6292(9)	5.6(3)
C3	0.244(2)	0.0036(9)	0.756(1)	5.9(4)
C4	0.285(1)	0.1541(9)	0.749(1)	5.3(4)
C5	0.033(1)	0.2018(8)	0.762(1)	4.4(3)
C6	−0.120(2)	−0.0793(7)	0.754(1)	5.1(3)
C7	−0.091(2)	−0.084(1)	0.6566(8)	10.3(5)
C8	−0.264(2)	−0.1072(8)	0.783(2)	8.8(5)
C9	−0.012(2)	−0.1238(9)	0.812(1)	7.5(5)
C10	−0.149(2)	−0.3503(9)	0.535(1)	5.9(4)
C11	−0.000(2)	−0.367(2)	0.550(1)	15.1(8)
C12	−0.220(3)	−0.424(1)	0.502(1)	13.1(7)
C13	−0.173(3)	−0.288(1)	0.466(1)	13.7(7)
C14	0.158(2)	0.3575(9)	1.032(1)	5.9(4)
C15	0.228(3)	0.311(1)	0.955(1)	11.0(7)
C16	0.012(1)	0.340(2)	1.042(1)	14.6(7)
C17	0.314(3)	−0.056(1)	0.490(2)	10.2(7)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3[a^2.B(1,1) + b^2.B(2,2) + c^2.B(3,3) + ab(\cos \gamma).B(1,2) + ac.(\cos \beta).B(1,3) + bc(\cos \alpha).B(2,3)])$

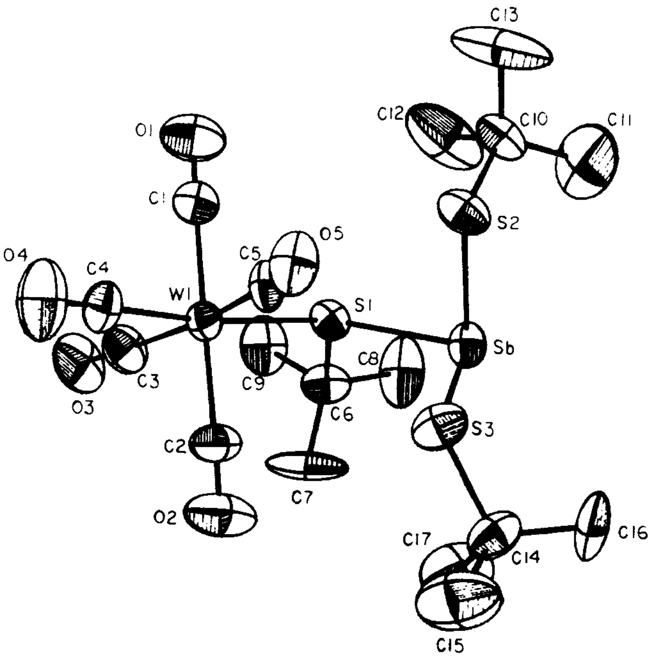

FIGURE 1 Ortep view of (1) showing the atom numbering scheme.

The geometry about Sb shows a significant distortion from the idealized tetrahedral value for an sp^3 hybridized Sb atom. Thus, S(1)-Sb-S(2) = 90.75(6)°, S(1)-Sb-S(3) = 90.95(6)° and S(2)-Sb-S(3) = 102.44(6)°. The geometry suggests that there is very little sp^3 hybridization for Sb with bonding to S occurring *via* P orbitals. The Sb lone pair thus has a large degree of s character and has relatively poor donor ability. The slightly larger angle subtended by the two non-bonded S atoms at Sb (S(2)-Sb-S(3)) could be due to relief of steric strain between their Bu^t groups since these S atoms are closer to Sb than S(1).

EXPERIMENTAL

General

All reactions were performed under oxygen-free nitrogen or under vacuum. Microanalyses were by the Schwartzkopf Microanalytical Laboratory, Woodside, NY. Hexane and THF were dried over sodium and distilled from sodium/benzophenone before use. $Sb(S\text{-}t\text{-}Bu)_3$ was prepared by the literature method.[4]

Instruments

IR; Perkin Elmer 1330; NMR; Varian EM-390 (^1H, 90 MHz)., NMR spectra are referenced to $Me_4Si(\delta\ 0.0, {}^1H)$. Melting points were measured in sealed capillaries under nitrogen (1 atm.) and are uncorrected.

Preparation of $(CO)_5W(\mu\text{-}S\text{-}Bu^t)Sb(S\text{-}Bu^t)_2$, (1)

A THF solution of $W(CO)_6$ (0.85 g, 2.4 mmol) and $Sb(S\text{-}Bu^t)_3$(0.93 g, 2.4 mmol) in a quartz Schlenk flask was photolyzed for five hours using a 550 W Hanovia mercury vapor lamp. The resulting red-brown solution was filtered and volatile materials were removed under vacuum. The residue was extracted with hexane ($2 \times 30\ cm^3$), filtered, and the yellow solution was reduced to 20 cm^3 in volume. Cooling to -20°C for 12 hours gives bright yellow crystals of (1); yield 0.95 g (57%); M.P. 95-100°C (dec.), ^1H NMR (in C_6D_6) δ 1.42 (s, 9H), δ 1.35 (s, 18H); IR (hexane solution, KBr plates) 2060 (s), 1983 (m), 1937 (s), 1920 (s) cm^{-1}. Anal. calcd. for $C_{17}H_{27}O_5S_3SbW$, C, 28.63; H, 3.82%; found C, 28.43; H, 3.55%.

X-Ray Experimental

Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated MoK_α radiation. Data were collected by the $\omega/2\theta$ scan technique at 23 ± 2°C. Details of the standard data collection methods were similar to those outlined in reference 8. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package "SDP-PLUS."[9]

A crystal of (1) was grown from a hexane solution at -20°C and mounted in a thin-walled glass capillary under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 22.0° and 24.0°. The monoclinic space group $P2_1/n$ (No. 1014) was uniquely determined by systematic absences. Data were collected in the ±*h*, +*k*, +*l* quadrant. Details of crystal data parameters and other relevant information are collected in Table I. The data were corrected for Lorentz and polarization effects and also for absorption using an empirical Ψ scan method (program EAC). A 0.8% decay of the standard reflections occurred, so no decay correction was applied. The observed structure factors of equivalent reflections were averaged. The structure was solved by direct methods (MULTAN)[10] followed by successive cycles of difference Fourier maps and least-squares refinement. A non-Poisson contribution weighting scheme with an experimental instability factor, *P*, was used in the final stages of refinement ($P = 0.05$).[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not located in the structure.

The maximum peak in the final difference Fourier map had a height of 0.66 eA^{-3} and was located 1.44 A from C(10). Scattering factors were taken from reference 12.

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SUPPLEMENTARY MATERIAL

Tables of thermal parameters and observed and calculated structure factors for (1) (33 pages) have been deposited with the editor and are available upon request.

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