

The Structure of μ -Oxo-bis[1,1,2-tricyanoethenoxy(triphenyl)antimony(III)] Benzene (2/1)

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Abstract. $[\text{Sb}(\text{C}_{23}\text{H}_{15}\text{N}_3\text{O})_2\text{O} \cdot \frac{1}{2}\text{C}_6\text{H}_6, \text{C}_{46}\text{H}_{30}\text{N}_6\text{O}_3 \cdot \text{Sb}_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6]$, monoclinic, $P2_1/c$, $a = 11.221(2)$, $b = 16.387(4)$, $c = 24.894(7)$ Å, $\beta = 100.41(2)^\circ$. There are four molecules of $[(\text{CN})_2\text{C}=\text{C}(\text{CN})\text{O}(\text{C}_6\text{H}_5)_3]_2\text{Sb}_2\text{O}$ and two molecules of solvent (benzene) per unit cell giving a density of 1.47 Mg m^{-3} . The approximate density measured by flotation is 1.5 Mg m^{-3} . Each molecule contains two O-bridged Sb atoms having approximately trigonal-bipyramidal geometry. There are phenyl groups in the three equatorial positions and O atoms in the two axial positions. One of these O atoms is bridging, and the other is in the $(\text{CN})_2\text{C}=\text{C}(\text{CN})\text{O}$ group.

Introduction. Weissenberg photographs showed $2/m$ Laue symmetry with systematic absences $k = 2n + 1$ for $0k0$ and $l = 2n + 1$ for $h0l$. The data were collected on an automated Picker diffractometer using the θ - 2θ scan technique with Zr-filtered Mo $K\alpha$ radiation. Each scan was 1.6° in 2θ with a counting time of 3 s per 0.05° step. A 30 s background was measured at the beginning and end of each scan. 5784 independent reflections were measured in the range $2\theta < 45^\circ$; 4870 reflections had $|F| \geq \sigma(F)$. The needle crystal used was $0.16 \times 0.17 \times 0.46$ mm. Absorption corrections were not applied ($\mu = 1.25 \text{ mm}^{-1}$). The estimated range of transmittance factors was 0.78 to 0.85. The Sb positions were found on a Patterson map. Successive electron density maps were used to find the remaining non-H atom positions. Difference maps did not show the locations of H atoms with any certainty. In the final cycle of full-matrix refinement using $|F| \geq \sigma(F)$ only Sb and O atoms were refined anisotropically and H-atom contributions were not included. Refinement was halted at this point due to the computer cost for a structure of this size. $R = 0.105$ for all reflections and $R_w = 0.078$ for all reflections $\geq 1.0\sigma(F)$. These values are a little high as a result of not including H atoms, absorption corrections, and anisotropic temperature factors for most of the atoms. $\sigma(I)^2 = \text{TC} + 2.56\text{BC} + (0.04)^2 I^2$

where TC = total count, BC = total background count, and $I = \text{TC} - 1.6\text{BC}$. Scattering factors for neutral atoms were obtained from *International Tables for X-ray Crystallography* (1962). Anomalous terms were not included. Computer programs were part of a local library (Anderson, 1971; Caputo, 1975). The final positional parameters are listed in Table 1.†

Discussion. This work was an attempt to verify the tentative structure assigned to the 2:2 adduct of tetracyanoethylene (TCNE) and triphenylphosphine (TPP) prepared and characterized by Douglas (1972). Since suitable crystals could not be prepared, attempts were made to substitute As and Sb for the P atom. Needles of a modified Sb analog were obtained. Even though three O atoms replaced two CN^- groups of the original compound, the structure analysis was undertaken in hopes of gaining information about $(\text{TCNE} \cdot \text{TPP})_2$.

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33956 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

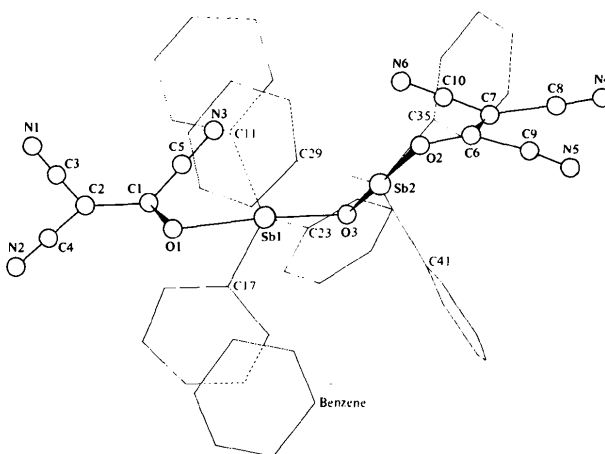


Fig. 1. One molecule of μ -oxo-bis[1,1,2-tricyanoethenoxy(triphenyl)antimony(III)] and one solvent molecule.

* Final data collection and computer analysis done at Washington State University, Pullman, on an NSF Small College Teacher Summer Research Grant.

Table 1. *Final atomic parameters (the standard deviation in the last digit is given in parentheses)*

	x	y	z		x	y	z
Sb(1)	0.57799 (7)	0.25678 (4)	0.24074 (3)	C(20)	0.686 (2)	0.4827 (9)	0.1338 (6)
Sb(2)	0.31257 (7)	0.21130 (5)	0.13455 (3)	C(21)	0.774 (2)	0.422 (1)	0.1494 (6)
O(1)	0.7773 (7)	0.2699 (4)	0.2890 (3)	C(22)	0.750 (1)	0.3536 (8)	0.1839 (5)
O(2)	0.2029 (7)	0.1594 (4)	0.0548 (3)	C(23)	0.525 (1)	0.2773 (6)	0.3158 (4)
O(3)	0.4077 (6)	0.2518 (4)	0.2023 (3)	C(24)	0.423 (1)	0.2334 (7)	0.3254 (5)
N(1)	1.093 (1)	0.1644 (8)	0.4204 (5)	C(25)	0.379 (1)	0.2463 (8)	0.3745 (6)
N(2)	1.073 (1)	0.3261 (7)	0.2810 (4)	C(26)	0.442 (1)	0.3028 (8)	0.4130 (5)
N(3)	0.737 (1)	0.1397 (8)	0.3878 (5)	C(27)	0.541 (1)	0.3452 (8)	0.4025 (5)
N(4)	-0.178 (1)	0.0910 (8)	-0.0513 (5)	C(28)	0.584 (1)	0.3322 (7)	0.3529 (4)
N(5)	-0.058 (1)	0.1933 (8)	0.1003 (6)	C(29)	0.452 (1)	0.1810 (6)	0.0918 (4)
N(6)	0.188 (1)	0.0751 (8)	-0.0741 (6)	C(30)	0.529 (1)	0.2424 (7)	0.0800 (5)
C(1)	0.841 (1)	0.2326 (7)	0.3277 (5)	C(31)	0.631 (1)	0.2195 (9)	0.0551 (6)
C(2)	0.963 (1)	0.2401 (6)	0.3402 (4)	C(32)	0.646 (1)	0.1383 (8)	0.0467 (5)
C(3)	1.035 (1)	0.1977 (9)	0.3853 (6)	C(33)	0.575 (1)	0.0744 (9)	0.0575 (6)
C(4)	1.025 (1)	0.2879 (7)	0.3078 (5)	C(34)	0.469 (1)	0.0980 (8)	0.0821 (3)
C(5)	0.786 (1)	0.1824 (9)	0.3612 (6)	C(35)	0.222 (1)	0.1230 (6)	0.1725 (4)
C(6)	0.092 (1)	0.1467 (8)	0.0352 (6)	C(36)	0.208 (1)	0.0425 (7)	0.1536 (5)
C(7)	0.045 (1)	0.1152 (8)	-0.0120 (6)	C(37)	0.145 (1)	-0.0130 (8)	0.1813 (5)
C(8)	-0.083 (2)	0.1065 (9)	-0.0319 (6)	C(38)	0.099 (1)	0.0122 (8)	0.2257 (5)
C(9)	-0.001 (1)	0.1703 (9)	0.0695 (6)	C(39)	0.114 (1)	0.0928 (8)	0.2449 (5)
C(10)	0.127 (2)	0.0942 (9)	-0.0451 (6)	C(40)	0.174 (1)	0.1489 (7)	0.2175 (5)
C(11)	0.634 (1)	0.1376 (7)	0.2229 (4)	C(41)	0.218 (1)	0.3221 (6)	0.1167 (4)
C(12)	0.739 (1)	0.1274 (8)	0.2007 (5)	C(42)	0.172 (1)	0.3432 (7)	0.0625 (5)
C(13)	0.768 (1)	0.0482 (8)	0.1850 (5)	C(43)	0.104 (1)	0.4159 (8)	0.0531 (5)
C(14)	0.695 (1)	-0.0154 (9)	0.1949 (6)	C(44)	0.087 (1)	0.4635 (8)	0.0967 (6)
C(15)	0.587 (1)	-0.0051 (8)	0.2138 (5)	C(45)	0.135 (1)	0.4429 (8)	0.1516 (5)
C(16)	0.557 (1)	0.0760 (7)	0.2307 (5)	C(46)	0.202 (1)	0.3699 (7)	0.1615 (5)
C(17)	0.634 (1)	0.3543 (6)	0.1973 (4)	C(47)	0.536 (2)	0.423 (1)	-0.0188 (6)
C(18)	0.545 (1)	0.4141 (8)	0.1793 (5)	C(48)	0.425 (2)	0.432 (1)	-0.0023 (6)
C(19)	0.575 (1)	0.4808 (9)	0.1472 (6)	C(49)	0.387 (1)	0.509 (1)	0.0161 (6)

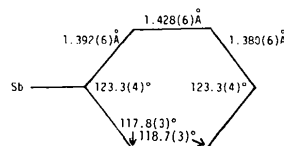
Table 2. *Bond lengths (Å) (the standard deviation in the last digit is given in parentheses)*

Left side Fig. 1	Right side Fig. 1
Sb(1)—O(3)	1.978 (8)
Sb(1)—O(1)	2.350 (9)
O(1)—C(1)	1.25 (2)
C(1)—C(2)	1.36 (2)
C(2)—C(3)	1.44 (2)
C(2)—C(4)	1.40 (1)
C(1)—C(5)	1.39 (2)
N(1)—C(3)	1.13 (2)
N(2)—C(4)	1.12 (1)
N(3)—C(5)	1.17 (2)
Sb(1)—C(11)	2.12 (1)
Sb(1)—C(17)	2.09 (1)
Sb(1)—C(23)	2.09 (1)
Sb(2)—O(3)	1.943 (7)
Sb(2)—O(2)	2.302 (8)
O(2)—C(6)	1.26 (2)
C(6)—C(7)	1.30 (2)
C(7)—C(8)	1.44 (3)
C(7)—C(10)	1.38 (2)
C(6)—C(9)	1.52 (2)
N(4)—C(8)	1.12 (2)
N(6)—C(10)	1.13 (2)
N(5)—C(9)	1.15 (2)
Sb(2)—C(29)	2.10 (1)
Sb(2)—C(35)	2.09 (1)
Sb(2)—C(41)	2.11 (1)

Each complex molecule (see Fig. 1) contains two approximately trigonal-bipyramidal Sb atoms bridged by an O atom through one axial position. The three phenyl groups on each Sb are in the equatorial positions and the remaining axial position is filled by an O that has replaced one of the cyano groups on the TCNE. The solvate benzene molecules are located on the centers at $\frac{1}{2}, \frac{1}{2}, 0$ and $\frac{1}{2}, 0, \frac{1}{2}$. Bond lengths in the benzene molecules are normal. Other bond lengths are listed in Table 2. The C—O bond lengths (1.25 and

1.26 Å) are unrealistically short (being the same as that of a carbonyl group) while the non-bridging Sb—O bonds (2.35 and 2.30 Å) fall outside the normal Sb—O bond range (1.89–2.27 Å) indicating the O atom positions may actually be closer to the Sb atoms. The bridging Sb—O bond lengths are normal. The C(6)—C(9) bond (1.52 Å) is suspiciously long compared to the five other similar bonds (average 1.41 Å).

The phenyl groups show distortion from D_{6h} symmetry. The average bond lengths and angles for all six phenyl groups are shown below.



The angle at the C atom attached to Sb of 123.3° puts the group attached to the phenyl ring among the strongly electron-withdrawing groups listed by Domenicano, Mazzeo & Vacigo (1976).

Bond angles in the benzene are normal. Other angles are listed in Table 3. The complex molecule seems to involve some steric hindrance, as there is distortion from what would be expected. All six phenyl groups are bent away from the equatorial positions toward the

Table 3. Bond angles (°) (the standard deviation in the last digit is given in parentheses)

Sb(1)—O(3)—Sb(2) 140.0 (3)			
Left side Fig. 1		Right side Fig. 1	
O(1)—Sb(1)—O(3)	176.6 (3)	O(3)—Sb(2)—O(2)	178.2 (3)
C(1)—O(1)—Sb(1)	135.1 (7)	Sb(2)—O(2)—C(6)	136.7 (7)
O(1)—C(1)—C(5)	120 (1)	O(2)—C(6)—C(9)	118 (1)
O(1)—C(1)—C(2)	123 (1)	O(2)—C(6)—C(7)	128 (1)
C(2)—C(1)—C(5)	117 (1)	C(7)—C(6)—C(9)	114 (1)
C(1)—C(2)—C(3)	123 (1)	C(6)—C(7)—C(8)	124 (1)
C(1)—C(2)—C(4)	120 (1)	C(6)—C(7)—C(10)	116 (1)
C(3)—C(2)—C(4)	117 (1)	C(8)—C(7)—C(10)	120 (1)
C(2)—C(3)—N(1)	179 (1)	C(7)—C(8)—N(4)	171 (2)
C(2)—C(4)—N(2)	179 (1)	C(7)—C(10)—N(6)	176 (2)
C(1)—C(5)—N(3)	178 (2)	C(6)—C(9)—N(5)	170 (2)
C(11)—Sb(1)—O(1)	84.3 (4)	C(29)—Sb(2)—O(2)	78.8 (4)
C(17)—Sb(1)—O(1)	81.1 (4)	C(35)—Sb(2)—O(2)	84.6 (4)
C(23)—Sb(1)—O(1)	85.8 (4)	C(41)—Sb(2)—O(2)	88.0 (4)

bridging O atom by an average of 6.2°. The angles around the O atoms are normal: Sb(1)—O(3)—Sb(2), 140.0°; C(1)—O(1)—Sb(1), 135.1°; Sb(2)—O(2)—

C(6), 136.7°. This structure sheds no light on the (TCNE.TPP)₂ structure, since the bonding between groups is through O atoms that are not present in the other adduct.

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Structure of the Potassium Methoxide Adduct of *s*-Trinitrobenzene, a Meisenheimer Complex

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Abstract. K(C₇H₆N₃O₇)·½H₂O, C₇H₆KN₃O₇·½H₂O, *M*_r = 292.3, monoclinic, *C*2/*c*, *a* = 12.411 (2), *b* = 9.051 (2), *c* = 19.565 (3) Å, β = 101.50 (2)°, *Z* = 8, *D*_x = 1.803 Mg m⁻³ (not measured). Data were collected on a computer-controlled four-circle diffractometer (Mo *K*α radiation, λ = 0.71069 Å, graphite monochromator), *F*(000) = 1192, μ(Mo *K*α) = 0.390 mm⁻¹. Final *R* = 0.045 for 2999 observed (*I* > 0) reflexions, 0.049 including unobserved. The methoxy group is covalently bound to the ring of *s*-trinitrobenzene at a C atom which attains tetrahedral (*sp*³) configuration. To relieve overcrowding between OCH₃ and the two neighbouring nitro groups, the anion assumes a butterfly shape.

Introduction. Meisenheimer complexes, the covalently-bound addition products resulting from reactions of aromatic nitro compounds with bases or other nucleo-

philic species, have been extensively studied by spectroscopic methods (for a review see Crampton, 1969). The molecular geometry of some of them has also been elucidated by X-ray diffraction. To our knowledge, the X-ray structure determinations so far reported concern only dialkoxy adducts, *i.e.* complexes derived from addition of an alkoxide ion to a benzene ring at a position which already carries an alkoxy group. They include: 1,1'-diethoxy-2,4,6-trinitrobenzene potassium or caesium (KDETNB; Destro, Gramaccioli & Simonetta, 1968); 1,1'-dimethoxy-2,4,6-trinitrobenzene potassium dihydrate (KDMTNB; Ueda, Sakabe, Tanaka & Furusaki, 1968); and 4,4'-dimethoxy-5,7-dinitrobenzofurazan (KDMDNBF; Messmer & Palenik, 1971). The present work is the first crystallographic study of an unsymmetrically substituted complex, obtained by addition of a methoxide ion to *s*-trinitrobenzene. Methanolic solutions of the adduct have been