Preparation and Structure of a Manganese Antimony μ_5-Oxo Ethoxide, $Mn_8Sb_4(\mu_5\text{-}O)_4(\mu_3\text{-}OEt)_4(\mu\text{-}OEt)_{16}$

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A new bimetallic manganese antimony ethoxide has been prepared by reacting anhydrous $MnCl_2$ with $NaSb(OEt)_4$ in a toluene/ethanol solution under inert atmosphere. Single-crystal X-ray diffraction investigations carried out at −103 °C show that the molecular formula of the ethoxide is $Mn_8Sb_4O_4(OEt)_{20}$. The compound crystallizes with space group symmetry *C2/c* and with the unit cell parameters $a = 17.565(6)$ Å, $b = 17.578(7)$ Å, $c = 21.870(5)$ Å, $\beta = 93.37(5)°$, and $Z = 4$. The crystal structure model was refined to an R value of 0.050 ($R_w = 0.062$) against the 3393 most significant reflections. The packing of the rather spherically shaped molecules in the crystal structure can be described as being approximately body-centered cubic. The molecular geometry has an approximate S_4 point symmetry. The antimony(III) atoms are five-coordinated by oxygen atoms. Four of the manganese(II) atoms are approximately octahedrally coordinated, while the remaining four manganese atoms are five-coordinated with a distorted square pyramidal coordination. Four of the oxygen atoms are of μ_5-oxo type with a coordination geometry of distorted square pyramids.

Introduction

Heterometallic alkoxides have become important in the development of new ceramic materials for the application of sol−gel techniques using alkoxides as precursors. To understand the reaction mechanisms occurring, it is important to know the structures of the molecular species involved. Structure investigations of such species are therefore a vital necessity. Many structural investigations have been performed on metal alkoxides in general, but the information about the structure of heterometallic alkoxides is more limited.[1,2]

The number of published studies concerning antimony(III)-containing bimetallic ethoxides is limited, and only some of them describe the molecular structure: $NaSb(OEt)_4$,[3] $Sn_3Sb(OEt)_{11}$,[4] $SnSb_2(OEt)_8$,[5] $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$,[6] $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$,[7] $Mg_2Sb_4(OEt)_{16}$,[8] $Sr_2Sb_4O(OEt)_{14}$,[9] $Ni_2Sb_4(OEt)_{16}$,[10] and $Mn_2Sb_4(OEt)_{16}$.[10] To obtain information about the heterometallic alkoxides, it is of interest to characterize as many as possible of the intermediate species in the same system. The Ni(II)−Sb(III) ethoxides mentioned above are isolated and characterized intermediates of a hydrolysis study[11] of the Ni(II)−Sb(III) ethoxide system. The compound presented in this paper is a newly characterized intermediate in the hydrolysis series of the Mn(II)−Sb(III) ethoxide system, which also contains other isolated species. The present study is part of a research project concerning the synthesis,[12] structural characterization, and study of the sol−gel process of bimetallic antimony(III) ethoxides containing divalent transition metal and alkaline earth ions.

Experimental Section

Preparation. All preparations and the mounting of crystals for the X-ray data collection were performed in a glovebox under dry, oxygen-free nitrogen atmosphere. The solvents used, toluene and ethanol, were dried with Na and CaH_2, respectively. $Sb(OEt)_3$ was prepared by reacting $SbCl_3$ with NH_3 gas in an ethanol−hexane mixture (40:60 vol %).[13] The crude $Sb(OEt)_3$ formed after evaporation of the hexane phase was purified by distillation in vacuum.

A 0.807 g amount of Na(s) was dissolved in a mixture of 60 mL of toluene and 16 mL of ethanol, followed by the addition of 9.01 g of liquid $Sb(OEt)_3$. The following day, 2.208 g of anhydrous $MnCl_2$ was added, and the mixture was allowed to react for 1 week at room temperature, giving a pale pink solution and precipitated NaCl. On slow evaporation of the solution and successive additions of a ethanol richer toluene−ethanol solution in order to keep the toluene:ethanol ratio (4:1) as constant as possible during the crystalization process, orange crystal plates were formed. The compound is very sensitive to moisture and to oxygen.

Structure Determination. Crystals of $Mn_8Sb_4O_4(OEt)_{20}$ with suitable dimensions were selected and mounted into glass capillaries (o.d. = 0.5 mm) within a glovebox under nitrogen atmosphere. The finally selected crystal was transferred to a STOE four-circle single-crystal X-ray diffractometer, equipped with a cryostat (N_2 gas stream) operating at 170 K. Preliminary investigations indicated a monoclinic space group symmetry. The θ values (14−27°) of 18 well-centered reflections were used to refine the cell parameters of the monoclinic unit cell (Table 1). The intensity data were corrected for background, Lorentz, polarization, and absorption effects. Systematic extinctions among the diffraction data indicated the possible space group symmetries *C2/c* and *Cc*. Subsequent studies of the intensity statistics clearly supported a centrosymmetric space group symmetry (*C2/c*).

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Table 1. Crystallographic Data for $\mathrm{Mn_8Sb_4O_4(OEt)_{20}}$

$\mathrm{Mn_8Sb_4O_4(OEt)_{20}}$	space group: *C*2/*c* (No. 15)
$M_r = 1891.7$	$T = 170(1)$ K
$a = 17.565(6)$ Å	$\lambda = 0.710\,73$ Å
$b = 17.578(7)$ Å	$\varrho_{calcd} = 1.864(2)$ g·cm^{-3}
$c = 21.870(5)$ Å	$\mu = 30.4$ cm^{-1}
$\beta = 93.37(5)°$	$R^a = 0.050$
$V = 6741(4)$ Å^3	$R_w{}^b = 0.061$
$Z = 4$	$R_w{}^c = 0.063$

[a] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma(w(\Delta F)^2)/\Sigma(wF_o{}^2)]^{-1/2}$. [c] Final R_w for all 4365 reflections.

Table 2. Fractional Atom Coordinates (×10^4) and Isotropic Thermal Parameters from the Refined Anisotropic Parameters (×10^3) for Non-Hydrogen Atoms (with Esd's) for $\mathrm{Mn_8Sb_4O_4(OEt)_{20}}$

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Sb(1)	437(1)	1101(1)	4048(1)	23(1)
Sb(2)	1735(1)	3477(1)	1869(1)	24(1)
Mn(1)	1221(1)	2302(1)	3028(1)	21(1)
Mn(2)	−1150(1)	1725(1)	3373(1)	23(1)
Mn(3)	−129(1)	2869(1)	3817(1)	23(1)
Mn(4)	0	941(1)	2500	23(1)
Mn(5)	0	3647(1)	2500	21(1)
O(1)	−861(4)	2836(4)	2943(3)	22(2)
O(2)	118(4)	1765(4)	3361(3)	21(2)
O(3)	−693(4)	3376(4)	1657(3)	20(2)
O(4)	−1219(4)	1254(4)	2526(3)	23(2)
O(5)	−1029(4)	3561(4)	3989(3)	29(2)
O(6)	−933(4)	4299(4)	2787(3)	26(2)
O(7)	−2140(4)	2967(4)	2254(3)	27(2)
O(8)	−2082(4)	2379(4)	3530(3)	34(3)
O(9)	−809(4)	1010(4)	4077(3)	32(2)
O(10)	289(4)	296(4)	3287(3)	31(2)
O(11)	1512(4)	1635(4)	3823(3)	26(2)
O(12)	230(4)	2170(4)	4530(3)	28(2)
C(3a)	−1165(6)	3983(7)	1391(5)	29(4)
C(3b)	−1434(7)	3813(8)	751(6)	39(4)
C(4a)	−1821(6)	719(7)	2369(5)	30(4)
C(4b)	−1871(7)	108(8)	2852(6)	40(4)
C(5a)	−1399(7)	3729(8)	4546(5)	41(4)
C(5b)	−1030(10)	4383(10)	4874(7)	66(6)
C(6a)	−1090(7)	5077(6)	2876(5)	32(4)
C(6b)	−495(8)	5479(8)	3258(7)	46(5)
C(7a)	−2938(6)	2892(7)	2146(5)	35(4)
C(7b)	−3224(8)	3173(9)	1546(6)	49(5)
C(8a)	−2722(7)	2292(8)	3886(6)	43(4)
C(8b)	−3262(8)	1729(10)	3634(7)	59(6)
C(9a)	−1097(9)	865(14)	4654(7)	84(8)
C(9b)	−1734(9)	392(12)	4668(7)	72(7)
C(10a)	146(9)	−480(8)	3470(6)	51(5)
C(10b)	844(11)	−930(11)	3471(11)	87(8)
C(11a)	2112(6)	1587(7)	4283(5)	31(4)
C(11b)	2783(7)	1167(9)	4090(6)	44(5)
C(12a)	533(10)	2239(9)	5147(6)	60(6)
C(12b)	108(10)	2702(9)	5536(6)	59(6)

[a] U_{eq} was estimated as $^1/_3$[trace (**U**)].

Table 3. Selected Intramolecular Bond Distances (Å, with Esd's ~ 0.01 Å) between Non-Hydrogen Atoms for $\mathrm{Mn_8Sb_4O_4(OEt)_{20}}$

Sb(1)−O(2)	1.96	Mn(3)−O(1)	2.24	O(3)−C(3a)	1.45
Sb(1)−O(9)	2.20	Mn(3)−O(2)	2.24	O(4)−C(4a)	1.44
Sb(1)−O(10)	2.19	Mn(3)−O(3)	2.04	O(5)−C(5a)	1.44
Sb(1)−O(11)	2.19	Mn(3)−O(5)	2.05	O(6)−C(6a)	1.41
Sb(1)−O(12)	2.20	Mn(3)−O(12)	2.06	O(7)−C(7a)	1.42
				O(8)−C(8a)	1.41
Sb(2)−O(1)	1.97	Mn(4)−O(2)	2.38	O(9)−C(9a)	1.41
Sb(2)−O(5)	2.19	Mn(4)−O(2′)	2.38	O(10)−C(10a)	1.45
Sb(2)−O(6)	2.18	Mn(4)−O(4)	2.22	O(11)−C(11a)	1.42
Sb(2)−O(7)	2.20	Mn(4)−O(4′)	2.22	O(12)−C(12a)	1.43
Sb(2)−O(8)	2.22	Mn(4)−O(10)	2.10		
		Mn(4)−O(10′)	2.10	C(3a−C(3b)	1.48
Mn(1)−O(1)	2.37			C(4a)−C(4b)	1.51
Mn(1)−O(2)	2.31	Mn(5)−O(1)	2.33	C(5a)−C(5b)	1.48
Mn(1)−O(3)	2.23	Mn(5)−O(1′)	2.33	C(6a)−C(6b)	1.48
Mn(1)−O(4)	2.20	Mn(5)−O(3)	2.20	C(7a)−C(7b)	1.46
Mn(1)−O(7)	2.12	Mn(5)−O(3′)	2.20	C(8a)−C(8b)	1.46
Mn(1)−O(11)	2.14	Mn(5)−O(6)	2.13	C(9a)−C(9b)	1.40
		Mn(5)−O(6′)	2.13	C(10a)−C(10b)	1.46
Mn(2)−O(1)	2.24			C(11a)−C(11b)	1.47
Mn(2)−O(2)	2.23			C(12a)−C(12b)	1.42
Mn(2)−O(4)	2.03				
Mn(2)−O(8)	2.05				
Mn(2)−O(9)	2.05				

Preliminary positions of the antimony atoms were obtained by heavy-atom methods, using the program package SHELX-76.[14] The positions of the other non-hydrogen atoms were found after preliminary least-squares refinements from calculations of difference electron density ($\Delta\varrho$) maps. The hydrogen atom positions were derived by assuming ideal geometries of the methylene and methyl groups and assuming the methyl hydrogen atoms in staggered orientations. The isotropic thermal parameters for all the hydrogen atoms were refined by using two paramters: one thermal parameter common for the methylene and another one common for the methyl hydrogen atoms. Least-squares refinement of the final structural model, using atomic X-ray scattering factors for neutral atoms from ref 15, yielded an R value of 0.050 (R_w = 0.061). Further details on the structural investigation are given in Table 1. The final atomic coordinates of the non-hydrogen atoms, intramolecular bond distances, and intramolecular bond angles are listed in Tables 2 and 3. Bond distances, bond angles, and least-squares planes were calculated with the PLATON[16] and PARST[17] program packages.

IR Investigation. IR spectra were recorded with a Mattson Polaris FT-IR instrument in the frequency range 4000−400 cm^{-1}, using freshly prepared specimens of $\mathrm{Mn_8Sb_4O_4(OEt)_{20}}$ in KBr pellets and in ethanol−toluene solution. The vibrations of the ethyl groups appear in the spectra at higher wavenumbers (> 1200 cm^{-1}), while the vibrations of the carbon−oxygen (C−O) and metal−oxygen (M−O) bonds are found in the lower region (1200−400 cm^{-1}) (Figure 1.). The C−O stretches in the region 1200−800 cm^{-1} are similar to those observed for other ethoxide compounds.[7,9,18] The spectra (Figure 1) of the solid and the dissolved specimens are similar in the M−O region (700−400 cm^{-1}), indicating that the metal−oxygen core structure of the solid is mainly intact in solution.

Results and Discussion

The crystal structure (Figures 2 and 3) consists of rather globular-shaped molecules with the composition $\mathrm{Mn_8Sb_4O_4(OEt)_{20}}$. The packing of the molecules in the crystal structure can roughly be considered as body-centered cubic. The lack of any proper hydrogen bond donors suggests that the structure is held together mostly by van der Waals forces. Among the 12 metal atoms present in each molecule, there are 4 five-coordinated antimony(III) atoms, 4 five-coordinated manganese(II) atoms, Mn(2) and Mn(3), and 4 six-coordinated manganese(II) atoms. The 24 oxygen atoms can be classified into 4 μ_5-oxo oxygen atoms, 4 μ_3-oxygen atoms, and 16 μ-oxygens, and the complete formula can be written as $\mathrm{Mn_8Sb_4(\mu_5\text{-}O)_4(\mu_3\text{-}OEt)_4(\mu\text{-}OEt)_{16}}$. The metal−oxygen core structure of $\mathrm{Mn_8Sb_4O_4(OEt)_{20}}$ is closely related to those of $\mathrm{Pb_6Nb_4O_4(OEt)_{24}}$[19] and $\mathrm{Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4}$.[7]

The space group symmetry of the crystals implies a 2-fold rotation axis through the two manganese atoms, Mn(4) and Mn-

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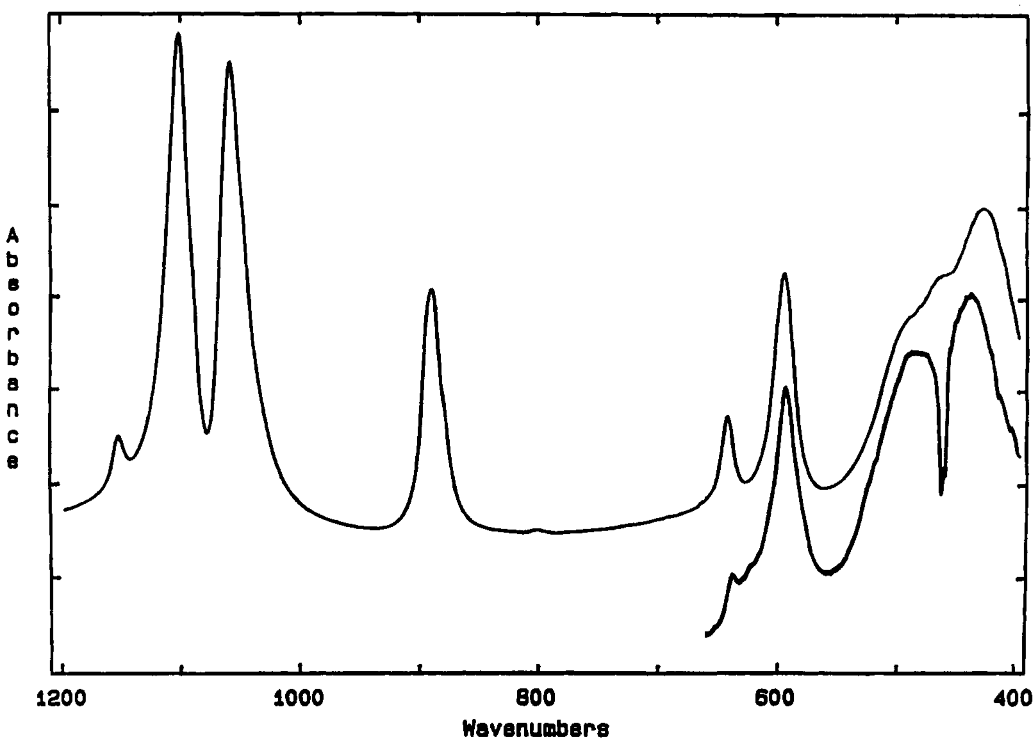

Figure 1. FT-IR spectra of $Mn_8Sb_4O_4(OEt)_{20}$: KBr tablet, upper; toluene–ethanol solution, lower. The extra dip at 470 cm^{-1} in the lower curve is due to solvent effects (toluene–ethanol).

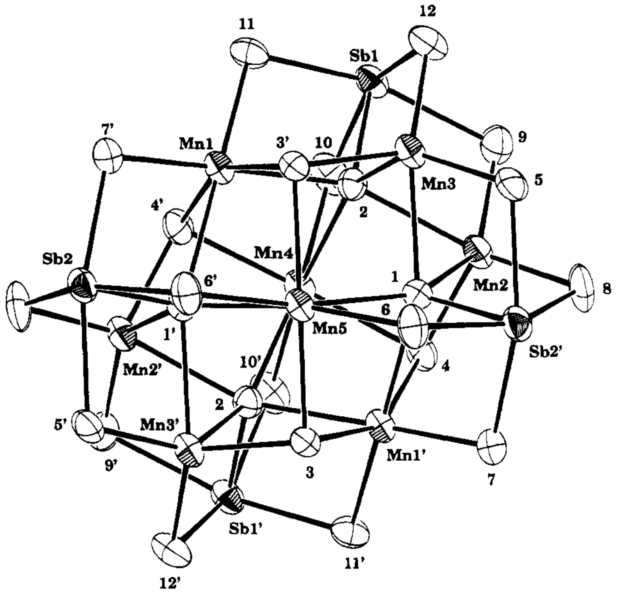

Figure 2. Labeled ORTEP drawing of the molecular structure of $Mn_8Sb_4O_4(OEt)_{20}$. The thermal ellipsoid sizes correspond to the 60% positional probability surface. The orientation is along the 2-fold rotation axis into the paper through Mn(5) and Mn(4). The antimony and manganese atoms are plotted with principal axes and octant shading of the ellipsoids while the oxygen atoms are plotted as ellipsoids with principal axes. Oxygen atoms are only labeled with numbers, and primed labels refer to atoms related by the 2-fold rotation symmetry. The ethoxy groups are omitted for clarity.

(5), located in the special positions (0, y, $^1/_4$) (see Figures 2 and 3). Due to this symmetry relation, the primed atoms in Figure 2 are symmetry equivalent to the unprimed ones. Apart from this exact C_2 point symmetry, the molecules have a noncrystallographic pseudo-S_4 point symmetry. The four antimony atoms are located at the surface of the molecule with their lone-pair regions (see below) pointing out from the surface. The oxygen atoms opposite the lone-pair directions of the antimony atoms are the μ_5-oxo oxygens, O(1) and O(2). Thus, the μ_5-oxo oxygens are located in the central region of the molecule, where they together with the five manganese atoms, Mn(1)–Mn(5), give rise to a void in the interior of the molecule. The two manganese atoms Mn(2) and Mn(3) are five-coordinated and have edge-shared coordination polyhedra, giving a short Mn••Mn distance of 2.86(1) Å. This short contact distance influences the shape of the molecule, and several bond and angle constraints are present. The configuration with the oxo oxygens opposite the antimony lone pair is commonly found in other structures containing antimony and oxo oxygens.[6–9] The presence of μ_5-oxo oxygen atoms in alkoxides is not that common.[20–27] The first μ_5-oxo oxygen atom in a alkoxide was found in 1986 in the structure of $(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu_3\text{-}OCH_3)_4(\mu_5\text{-}O)$.[20]

The antimony atoms Sb(1) and Sb(2) are coordinated by five oxygen atoms with a distorted octahedral coordination, where one of the apical positions opposite the oxo oxygens O(2) and O(1) apparently is occupied by the antimony lone pair. The average antimony–oxygen bond distances are 2.15 Å. The bond distances to the O(1) and O(2) oxo oxygen atoms are, as expected, significantly shorter (Table 3). Calculated empirical bond valence sums[28,29] (bvs) for the antimony atoms are about 3.2 and verify that the bond distance distributions agree with those commonly found for trivalent antimony ions.

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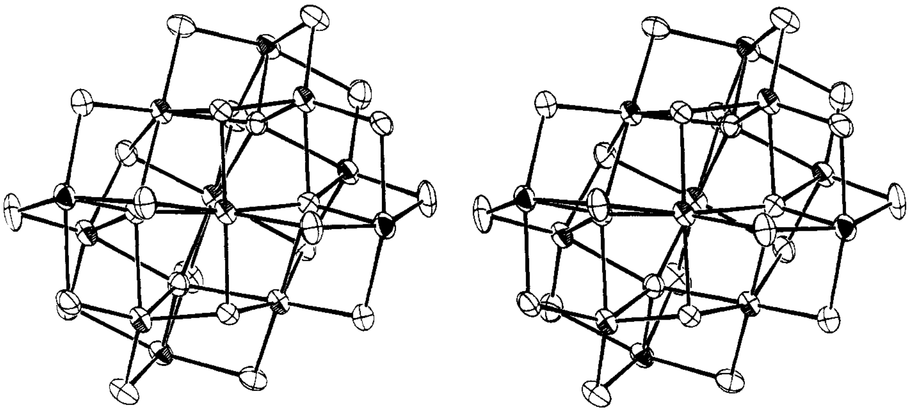

Figure 3. ORTEP stereo drawing of the molecular structure of $Mn_8Sb_4O_4(OEt)_{20}$, with the same orientation as Figure 2.

The manganese atoms Mn(1), Mn(4), and Mn(5) are coordinated to six oxygen atoms with distorted octahedral coordinations. The bond distances vary between 2.10(1) and 2.37(1) Å with average values 2.23(9), 2.23(12), and 2.22(9) Å, respectively. In general, the metal−oxygen bond distances increase with increased μ values of the oxygen atom. The bond valence sums for the Mn(1), Mn(4), and Mn(5) atoms are all about 1.9. The coordination geometries agree with those found in e.g. the structure of $Mn_2Sb_4(OEt)_{16}$.[10]

The coordination polyhedra around the five-coordinated manganese atoms Mn(2) and Mn(3) can be considered as distorted square pyramids. Two adjacent Mn(2) and Mn(3) polyhedra share a common edge, giving a Mn(2)···Mn(3) distance as short as 2.68(1) Å. Five-coordinations can often be considered as having an intermediate geometry between a trigonal bipyramid with D_{3h} symmetry and a square pyramid with C_{4v} symmetry. The transformation from a trigonal (D_{3h}) to a square pyramidal (C_{4v}) geometry can then be described with the linear Berry rearrangement[30,31] reaction coordinate. In the present case, geometrical constraints occur due to the shared coordination edge (*cf.* above), and the coordination geometries around Mn(2) and Mn(3) fall outside the ideal linear reaction path for a true Berry rearrangement. The oxygen atoms forming the square base planes around Mn(2) and Mn(3) are coplanar within 0.006(7) Å, with the two manganese atoms displaced by 0.556(2) and 0.595(2) Å, respectively, above the plane toward the apical oxygen atoms. The estimated bvs values for the two manganese atoms Mn(2) and Mn(3) are both about 2.1.

The two oxo atoms O(1) and O(2) are five-coordinated by metal ions in the shape of distorted square pyramids. Two (O(3) and O(4)) of the ten symmetry-independent ethoxy oxygen atoms are three-coordinated, while the remaining ones are two-coordinated. The ethoxy groups all have normal geometries, with average $O-C_\alpha$ and $C_\alpha-C_\beta$ bond distances of 1.43(2) and 1.46(3) Å and average $O-C_\alpha-C_\beta$ angles of 113(2)°.

The thermal vibrations of the molecule, as described by the obtained anisotropic displacement parameters, were analyzed for the presence of any pronounced rigid groups of atoms within in the molecule. This analysis, using the techniques as described by Hirshfeld[32] and Rosenfield *et al.*,[33] was confined to the metal and oxygen atoms. The results showed that some of the μ-oxygen atoms were involved in large differences of up to 0.02 $Å^2$, between the mean-square displacements of two atoms along the interatomic directions involved. Accordingly, these oxygen atoms were also excluded from any further analyses. For the remaining 20-atom molecular fragment ($Mn_8Sb_4O_8$), which included all metal atoms and the oxygen atoms with coordination number higher than 2, the mean-square displacements along interatomic directions became less than 0.006 $Å^2$. With the program THMA11,[34] the 12 independent parameters needed to describe the rigid-body thermal motions were determined from the 62 observed anisotropic displacement parameters. With the derived rigid-body model, all the observed parameters for the atoms in the fragment are all predicted within less than three esd's. The agreement between observed and predicted parameters (weighted R value 0.086) gives some support for the assumed rigidity of the central 20-atom $Mn_8Sb_4O_8$ fragment of the molecule. The corrections of the bond distances due to rigid-body motion are all negligible ($\leq$0.001 Å).

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Supplementary Material Available: Tables of crystallographic data, anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for the hydrogen atoms, and calculated bond distances and angles and two figures showing the molecular packing in the crystal structure (9 pages). Ordering information is given on any current masthead page.

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