Synthesis and Structural Investigation of a New Manganese–Antimony Oxoethoxide, $Mn_7Sb_4(\mu_5-O)_2(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OEt)_{16}(HOEt)_2$

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A new manganese–antimony oxoethoxide with the formula $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$ has been prepared and characterized by single-crystal X-ray diffraction and FT–IR techniques. The structure of the compound has the noncentrosymmetric tetragonal space group symmetry $P4_2$ (No. 77) with unit-cell parameters $a = 15.164(3)$, $c = 14.729(5)$ Å, $V = 3387(2)$ Å^3, $Z = 2$, and $D_x = 1.803(1)$ g cm^{-1} $F_w = 1838.8$ g mol^{-1}. The crystal structure has been refined against the 2227 most significant reflections to an R value of 0.059 ($R_w = 0.077$). The single-crystal X-ray diffraction intensities were collected at 170(1) K using Mo$K\alpha$ radiation. The structure analysis shows that the structure consists of roughly spherically shaped molecules of C_2 symmetry and of composition $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$. The antimony atoms are five-coordinated by oxygen atoms, while four of the manganese atoms are five-coordinated and three are six-coordinated. The antimony atoms are located in the outer regions of the molecule and the antimony lone pair regions are pointing away from the molecule. Four oxooxygens are located in the core of the molecule. The ethanol molecules coordinating the antimony atoms are involved in short intramolecular hydrogen bonds. A TLS analysis of the rigid-body motion of the central metal–oxygen core structure shows that two oxygen atoms involved in the intramolecular hydrogen bond do not follow the pattern of the rest of the atoms. The agreement between observed and predicted parameters of the remaining atoms supports the assumed rigidity in the central metal and oxygen core fragment. Structural relationships are found to other spherically shaped alkoxides such as $Mn_8Sb_4O_4(OEt)_{20}$ and $Pb_6Nb_4O_4(OEt)_{24}$.
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INTRODUCTION

Mixed metal oxides are important for the development of new materials with specific properties, e.g., electronic devices, sensors, and optical devices. In these kinds of ceramics it is important to have an extreme homogeneity, which can be hard to achieve using traditional synthetic routes. Heterometallic alkoxides can often be used as versatile precursors in sol–gel processes to obtain the desired homogeneity. Information on the molecular structures of the precursors and of the oxoalkoxides formed during the gelling process is of course of vital importance in understanding various physical and chemical properties and also in controlling the final product. Although one always must consider the possibility that the molecular structure in the solid state in some cases might differ from that in solutions, a determination of the crystal structure has the power of giving unambiguous structural formation (1–3).

Earlier studies by our group have been focused on the synthesis, structural characterization, and hydrolysis of antimony-containing bimetallic transition metal alkoxides. Thus several structures have been synthesized and characterized in the nickel(II)–antimony(III) ethoxide system (4–8) and in the manganese(II)–antimony(III) ethoxide system $Mn_2Sb_4(OEt)_{16}$ (6) and $Mn_8Sb_4O_4(OEt)_{20}$ (9).

In this article we present a new compound found in the manganese(II)–antimony(III) ethoxide system with the formula $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$.

EXPERIMENTAL

Preparation

All manipulations and the mounting of single crystals were performed in dry, oxygen-free nitrogen or argon atmosphere in a glove box. The ethanol and toluene were dried with CaH$_2$ and Na chips, respectively. The Sb(OEt)$_3$ was prepared from SbCl$_3$ in ethanol, which was treated with anhydrous ammonia gas (10) and distilled under vacuum, and the NaSb(OEt)$_4$ was prepared by dissolving Na$_{(S)}$ in ethanol and adding Sb(OEt)$_3$. The Mn$_2$Sb$_4$(OEt)$_{16}$ was prepared by adding MnCl$_{2(S)}$ to a NaSb(OEt)$_4$ solution (composition ratio 1:2) and allowing the solution to react for a number of days (6). The NaCl formed during the reaction precipitated and the

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weak pink solution was evaporated to a white crystalline mass.

$Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$ consists of pale orange crystals and can be prepared from $Mn_2Sb_4(OEt)_{16}$ in ethanol-rich toluene–ethanol solvents by self-decomposition over a period of several months or by hydrolysis with H_2O diluted in the toluene–ethanol solvent used. The hydrolysis was performed by dropwise addition of 1 M H_2O in toluene: ethanol (1:2 vol/vol), $h = 1.14$ ($h = H_2O/Mn_2Sb_4(OEt)_{16}$), to a vigorously stirred 0.18 M $Mn_2Sb_4(OEt)_{16}$ toluene: ethanol solution (1:2). Two hours after the addition of the water, the solvent was slowly removed stepwise by evaporation, and crystals of $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$ appeared after a number of days to a week. No other bimetallic alkoxides were found at this h value with the solvent. In toluene:ethanol (4:1) solvent, at $h = 1.14$, $Mn_8Sb_4O_4(OEt)_{20}$ (9) was formed instead. The compound differs from the similar $Mn_8Sb_4O_4(OEt)_{20}$ in its weaker color and different IR spectrum, i.e., the presence of a OH-stretch band and different C–O and M–O bands (see Fig. 1). The expected excess of antimony is found, by IR analysis, in the form of $Sb(OEt)_{3(1)}$ remaining in the solvent. The crystals had the shape of elongated plates, were of sizes from millimeters to centimeters, and had to be cut to sizes suitable for single-crystal studies.

FIG. 1. FT–IR spectra of the M–O bands of $Mn_8Sb_4O_4(OEt)_{20}$ (lower curve) and $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$ (upper curve).

Structural Determination

Suitable crystals mounted in capillaries were selected and put onto a STOE single-crystal X-ray diffractometer. Preliminary investigations indicated a primitive tetragonal space group symmetry. The unit-cell parameters were determined and refined from accurate diffractometer-determined θ values to be $a = 15.164(3)$ and $c = 14.729(5)$ Å. Single-crystal X-ray diffraction data were collected and corrected for background, Lorentz, polarization, and absorption effects. The possible space group symmetry was deduced from systematic extinctions among the diffraction data. The noncentrosymmetric (polar) space group symmetry $P4_2$ was indicated by intensity statistics and was fully supported by the outcome of the investigation. Further details on the experimental conditions are given in Table 1.

Preliminary Sb positions were obtained by the application of direct methods using the program package SHELXS-86 (11). The positions of the remaining nonhydrogen atoms were found from subsequent least-squares refinements and difference electron density ($\Delta\rho$) calculations. The origin along the polar z axis was defined by keeping the z coordinate of one of the symmetry-independent Sb atoms fixed at 0. Refining models of the two possible enantiomeric structures did not give any statistically relevant result that could indicate the most probable enantiomer. The ethoxy carbon atoms $C_\alpha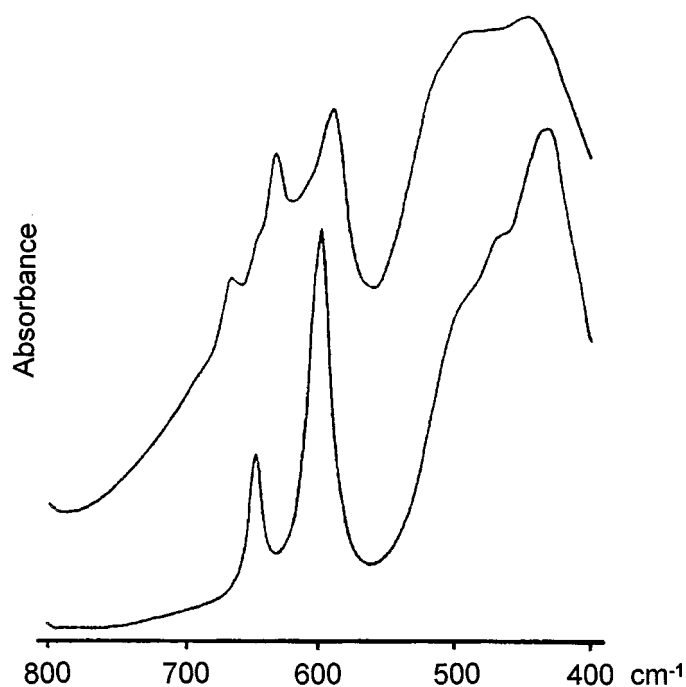$ and C_β were refined with a restrained ideal geometry, with the bond angle, $O-C_\alpha-C_\beta$, and the bond distances, $O-C_\alpha$ and $C_\alpha-C_\beta$, refined as free variables to $109.5°$, 1.46 Å, and 1.44 Å. The carbon atoms show large thermal motions and were refined with isotropic temperature parameters. The carbon atoms with the largest temperature parameters could possibly be expected to be disordered. However, it was not possible to find any significant peaks in the $\Delta\rho$ maps that indicated disorder. The hydrogen atoms were positioned with ideal geometry and refined by constraining them to geometrically predicted positions around the carbon atoms (C–H distances of 1.0 Å and bond angles of $109.5°$). Least-squares refinements of the structural model yielded a final R value of 0.059 (w$R = 0.077$).

The final atomic coordinates with isotropic thermal parameters, bond distances, and bond angles are listed in Tables 2–4. The methylene and methyl carbon atoms of the ethoxy groups have been labeled with the number of the ethoxy oxygen atoms followed by letters A and B, respectively. The structural refinements were carried out by means of the SHELX-76 (12) package using atomic scattering factors for neutral atoms from the International Tables for X-ray Crystallography (13). The programs PLATON (14) and PARST (15) have been used to derive molecular geometry such as distances, angles, and least-squares planes.

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TABLE 1
Experimental Conditions for $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$

Formula (X-ray study)	$Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$
Formula weight	$1838.8\,g\,mol^{-1}$
Space group	$P4_2$
Unit-cell dimensions	$a = 15.164(2)$, $c = 14.729(4)$ Å
Unit-cell volume, V	$3386.9(11)$ Å^3
Formula units per unit cell, Z	2
Calculated density, D	$1.8031(6)\,g\,cm^{-3}$
Radiation	$MoK\alpha$
Wavelength, λ	0.71073 Å
Temperature, T	$170(1)$ K
Crystal shape	Prismatic
Crystal size	$0.25 \times 0.26 \times 0.16\,mm$
Diffractometer	Stoe 4-circle
Determination of unit cell	
Number of reflections used	19
θ range	$10.1–14.5°$
Intensity data collection	ω-2θ scan technique.
Maximum $\sin(\theta)/\lambda$	0.76 Å^{-1}
Range of h, k, and l	0 to 22, 0 to 22, and 0 to 22
Standard reflections	(4 0 0), (0 4 0), and (0 0 4)
Intensity instability	$< 1.6\%$
Internal R	0.016
Number of collected reflections	6744
Number of unique reflections	6335
Number of observed reflections	2227
Criterion for significance	$I > 5 \cdot (\sigma(I))$
Absorption correction	Numerical integration
Linear absorbtion coefficient	$30.22\,cm^{-1}$
Transmission factor range	0.52–0.64
Structure refinement	Full–matrix least squares
Minimization of	$\sum w(\Delta F)^2$
Anisotropic thermal parameters	Mn, Sb, and O atoms
Isotropic thermal parameters	C and H atoms
Number of refined parameters	241
Weighting scheme	$(\sigma^2(F) + 0.0006 \cdot |F|^2)$
Final R^a for observed reflections	0.059
Final wR^b for observed relections	0.077
Final wR^b for all 6335 reflections	0.094
Final $(\Delta/\delta)_{max}$	0.012
Final $\Delta\rho_{max}$ and $\Delta\rho_{min}$	1.9 and -1.3 e$\cdot$Å^{-3}

[a] $R = (\sum \|F_o| - |F_c\|)/\sum|F_o|$.
[b] w$R = [\sum(w(\Delta F)^2)/\sum(wF_o^2)]^{-1/2}$.

TABLE 2
Fractional Atomic Coordinates ($\times10^4$) and Isotropic Thermal Parameters from the Refined Anisotropic Parameters ($\times10^3$) for Nonhydrogen Atoms (with e.s.d.'s) for $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$

Atom	x	y	z	$U_{eq}{}^a$
Sb(1)	$-1531(1)$	6552(1)	0	54(1)
Sb(2)	$-1230(1)$	6513(1)	3193(2)	59(1)
Mn(1)	0	5000	16(3)	35(1)
Mn(2)	1753(2)	5162(2)	1367(3)	44(1)
Mn(3)	236(2)	6700(2)	1231(3)	44(1)
Mn(4)	732(2)	4372(2)	2943(3)	53(1)
O(1)	586(8)	5730(9)	2364(9)	44(4)
O(2)	$-842(8)$	5883(8)	906(9)	37(4)
O(3)	1072(9)	5960(8)	414(9)	47(4)
O(4)	1987(9)	4087(13)	2435(12)	86(6)
O(5)	95(12)	3401(12)	3698(13)	89(7)
O(6)	866(10)	7469(8)	2208(11)	62(5)
O(7)	2461(9)	4511(10)	361(12)	65(5)
O(8)	$-446(10)$	7435(9)	278(11)	62(5)
O(9)	825(10)	4250(10)	$-868(10)$	53(5)
O(10)	2315(9)	6098(10)	2287(12)	68(5)
O(11)	1212(12)	5260(12)	3919(11)	75(6)
O(12)	$-2152(13)$	7113(13)	1489(16)	107(8)
C(3a)	1518(12)	6323(13)	$-379(13)$	49(5)
C(3b)	2175(14)	6981(14)	$-136(19)$	79(8)
C(4a)	2706(14)	4206(18)	3124(17)	88(8)
C(4b)	3557(14)	3976(23)	2722(23)	115(12)
C(5a)	429(22)	2577(16)	4078(17)	100(10)
C(5b)	397(25)	2550(22)	5055(17)	135(13)
C(6a)	$-1289(18)$	8310(15)	2184(30)	125(13)
C(6b)	718(24)	9061(15)	2182(28)	133(14)
C(7a)	3240(21)	4713(24)	$-207(28)$	160(17)
C(7b)	3910(24)	4059(36)	$-127(42)$	334(42)
C(8a)	$-505(21)$	8288(17)	$-167(24)$	133(13)
C(8b)	285(23)	8489(23)	$-682(28)$	146(15)
C(9a)	1060(23)	4308(26)	$-1835(17)$	143(15)
C(9b)	420(41)	3868(45)	$-2403(24)$	355(44)
C(10a)	3087(16)	6641(17)	2316(23)	105(10)
C(10b)	3875(17)	6319(24)	1955(30)	139(14)
C(11a)	1235(20)	5246(22)	4906(16)	113(11)
C(11b)	1965(29)	4749(35)	5268(26)	241(27)
C(12a)	$-1910(28)$	7978(25)	1807(45)	254(29)
C(12b)	$-2541(30)$	8452(22)	2320(30)	184(20)

[a] U_{eq} was estimated as $1/3[trace(\mathbf{U})]$.

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IR Investigation

Infrared spectra were recorded for KBr pellets in the range 4000–400 cm^{-1} using a Mattson Polaris FT–IR spectrometer. The most pronounced differences between M^{2+} and Sb^{3+} (oxo) ethoxides are normally found in the M–O band, which contains information from both the Sb–O and Mn–O–Sb bonds and is therefore a useful tool in distinguishing between the similar $Mn_7Sb_4O_4(OEt)_{18}$ (HOEt)$_2$ and $Mn_8Sb_4O_4(OEt)_{20}$ formed in about the same range of hydrolysis, but with different solvents. The M–O bands of $Mn_8Sb_4O_4(OEt)_{20}$ (lower curve) and $Mn_7Sb_4O_4(OEt)_{18}$

(HOEt)$_2$ (upper curve) are shown in Fig. 1. Here it can be observed that $Mn_7Sb_4O_4(OEt)_{18}$ (HOEt)$_2$, which has the more complex structure with two different Sb ion coordinations and which contains OH bonds, also yields the more complex M–O band. The peak maxima of $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$ in the C–O and M–O regions (1200–400 cm^{-1}) are found at 449, 479, 589, 629, 664, 893, 1060, 1100, and 1155 cm^{-1}.

The OH stretch band is weak and very broad, which makes it difficult to give an accurate band maximum, about

TABLE 3
Selected Intramolecular Bond Distances (with e.s.d.'s between Nonhydrogen Atoms for $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$

Sb(1)–O(2)	1.98(2)	Sb(2)–O(1)	1.96(2)
Sb(1)–O(9)'	2.07(2)	Sb(2)–O(6)	2.12(2)
Sb(1)–O(8)	2.16(2)	Sb(2)–O(5)'	2.15(2)
Sb(1)–O(7)'	2.21(2)	Sb(2)–O(11)	2.18(2)
Sb(1)–O(12)	2.53(2)	Sb(2)–O(10)	2.21(2)
Mn(1)–O(9)	2.14(2)	Mn(2)–O(7)	2.08(2)
Mn(1)–O(9)'	2.14(2)	Mn(2)–O(3)	2.12(2)
Mn(1)–O(3)	2.26(2)	Mn(2)–O(10)	2.14(2)
Mn(1)–O(3)'	2.26(2)	Mn(2)–O(2)'	2.21(2)
Mn(1)–O(2)	2.27(2)	Mn(2)–O(4)	2.29(2)
Mn(1)–O(2)'	2.27(2)	Mn(2)–O(1)	2.46(2)
Mn(3)–O(8)	2.07(2)	Mn(4)–O(5)	2.08(2)
Mn(3)–O(3)	2.08(2)	Mn(4)–O(4)	2.09(2)
Mn(3)–O(6)	2.08(2)	Mn(4)–O(11)	2.10(2)
Mn(3)–O(2)	2.11(2)	Mn(4)–O(1)'	2.18(2)
Mn(3)–O(1)	2.29(2)	Mn(4)–O(1)	2.24(2)

$2600-2500 \text{ cm}^{-1}$, comparable to those of $Ni_5Sb_3O_2(OEt)_{15}$ $(HOEt)_4$ (4) $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$ (5), which have maxima at about $2540-2520 \text{ cm}^{-1}$ for $O \cdots O$ hydrogen bond distances of about 2.5 Å. Thus, a very strong $O-H \cdots O$ bond may be assumed.

RESULTS AND DISCUSSION

The roughly spherical molecules can be considered an approximately body-centred cubic packed in the crystal structure, with two molecules in each unit cell. There are no intermolecular hydrogen bonds present and the structure is held together mostly by van der Waals forces with a shortest intermolecular distance of 3.62(7) Å between nonhydrogen atoms. Each molecule consists of 7 manganese atoms, 4 antimony atoms, 4 oxooxygens and 20 ethoxy groups.

Taking the bond distributions into account and calculating empirical bond valence sums (16, 17) verify that the manganese atoms are divalent and that the antimony atoms are trivalent. To achieve electroneutrality within each molecule, two of the ethoxy groups must be protonated. A weak OH stretch band is also observed in FT–IR. The molecular formula will thus be $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$. By taking the metal coordination around the oxygen atoms into account, the formula can be written as $Mn_7Sb_4(\mu_5-O)_2$ $(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OEt)_{16}(HOEt)_2$.

The molecule has a crystallographic twofold rotation symmetry. The symmetry-generated atoms in Figs. 2 and 3 have primed labels. The molecular conformation shows similarities to the previously known structure of $Mn_8Sb_4O_4(OEt)_{20}$ (9). The central core metal–oxygen skeleton is roughly the same but two five-coordinated

TABLE 4
Selected Bond Angles (with e.s.d.'s) for Nonhydrogen Atoms for $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$

O(2)–Sb(1)–O(9)'	80.9(6)	O(1)–Sb(2)–O(6)	81.9(6)
O(2)–Sb(1)–O(8)	77.7(5)	O(1)–Sb(2)–O(5)'	77.7(6)
O(2)–Sb(1)–O(7)'	78.4(5)	O(1)–Sb(2)–O(11)	76.8(6)
O(2)–Sb(1)–O(12)	77.5(6)	O(1)–Sb(2)–O(10)	79.8(5)
O(9)'–Sb(1)–O(8)	95.0(6)	O(6)–Sb(2)–O(5)'	87.2(7)
O(9)'–Sb(1)–O(7)'	92.9(6)	O(6)–Sb(2)–O(10)	88.6(6)
O(9)'–Sb(1)–O(12)	157.9(6)	O(6)–Sb(2)–O(11)	157.9(6)
O(8)–Sb(1)–O(7)'	153.3(6)	O(5) '–Sb(2)–O(10)	157.5(6)
O(8)–Sb(1)–O(12)	84.9(6)	O(5) '–Sb(2)–O(11)	82.6(7)
O(7)'–Sb(1)–O(12)	78.4(5)	O(11)–Sb(2)–O(10)	93.3(6)
O(9)'–Mn(1)–O(9)	104.7(6)	O(7)–Mn(2)–O(1)	164.8(5)
O(9)'–Mn(1)–O(2)	73.0(5)	O(7)–Mn(2)–O(3)	92.9(6)
O(9)–Mn(1)–O(3)	94.6(5)	O(7)–Mn(2)–O(10)	124.1(6)
O(9)–Mn(1)–O(3)'	103.7(5)	O(7)–Mn(2)–O(2)'	76.3(5)
O(9)–Mn(1)–O(2)	176.0(5)	O(7)–Mn(2)–O(4)	94.1(6)
O(3)–Mn(1)–O(3)'	149.9(5)	O(3)–Mn(2)–O(1)	81.1(5)
O(3)–Mn(1)–O(2)'	79.9(5)	O(3)–Mn(2)–O(10)	103.6(6)
O(3)–Mn(1)–O(2)	82.8(5)	O(3)–Mn(2)–O(2)'	84.4(5)
O(2)'–Mn(1)–O(2)	109.4(5)	O(3)–Mn(2)–O(4)	159.2(5)
		O(10)–Mn(2)–O(1)	71.1(5)
		O(10)–Mn(2)–O(2)'	156.9(6)
		O(10)–Mn(2)–O(4)	88.6(6)
		O(2)'–Mn(2)–O(1)	89.2(5)
		O(2)'–Mn(2)–O(4)	78.3(5)
		O(4)–Mn(2)–O(1)	87.2(5)
O(8)–Mn(3)–O(3)	101.7(6)	O(5)–Mn(4)–O(4)	117.9(7)
O(8)–Mn(3)–O(6)	113.4(6)	O(5)–Mn(4)–O(11)	104.4(7)
O(8)–Mn(3)–O(2)	76.9(5)	O(5)–Mn(4)–O(1)'	74.5(6)
O(8)–Mn(3)–O(1)	163.2(5)	O(5)–Mn(4)–O(1)	143.8(6)
O(3)–Mn(3)–O(6)	115.0(6)	O(4)–Mn(4)–O(11)	93.6(7)
O(3)–Mn(3)–O(2)	91.4(5)	O(4)–Mn(4)–O(1)'	132.9(6)
O(3)–Mn(3)–O(1)	86.2(5)	O(4)–Mn(4)–O(1)	98.3(6)
O(6)–Mn(3)–O(2)	147.3(6)	O(11)–Mn(4)–O(1)'	129.2(6)
O(6)–Mn(3)–O(1)	75.5(5)	O(11)–Mn(4)–O(1)	72.9(6)
O(2)–Mn(3)–O(1)	88.1(5)	O(1) '–Mn(4)–O(1)	80.0(5)

manganese atoms in $Mn_8Sb_4O_4(OEt)_{20}$ are replaced by one six-coordinated manganese atom, Mn(1), in $Mn_7Sb_4O_4(OEt)_{18}$ $(HOEt)_2$. The other metal atoms in the core skeleton all lie in similar relative positions as in $Mn_8Sb_4O_4(OEt)_{20}$. The oxygen atom positions differ of course a little more. Structural resemblances can also be found to the structures of $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$ (5), $Pb_6Nb_4O_4(OEt)_{24}$ (18), and the decanuclear mixed-valent $Mn(II)_6Mn(III)_4$ complex studied by Goldberg et al. (19)

The Sb(1) and Sb(2) atoms in $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$ are both five-coordinated as square pyramids, with the antimony (III) lone pair located opposite to the oxooxygen and pointing out from the molecule. The antimony bond distances vary between 1.98–2.53 and 1.96–2.21 Å, respectively (see Table 3), with bond distance averages of 2.2(2) and 2.1(1) Å. The calculated empirical bond valence sums (bvs values) for the antimony atoms are 3.1 and 3.4,
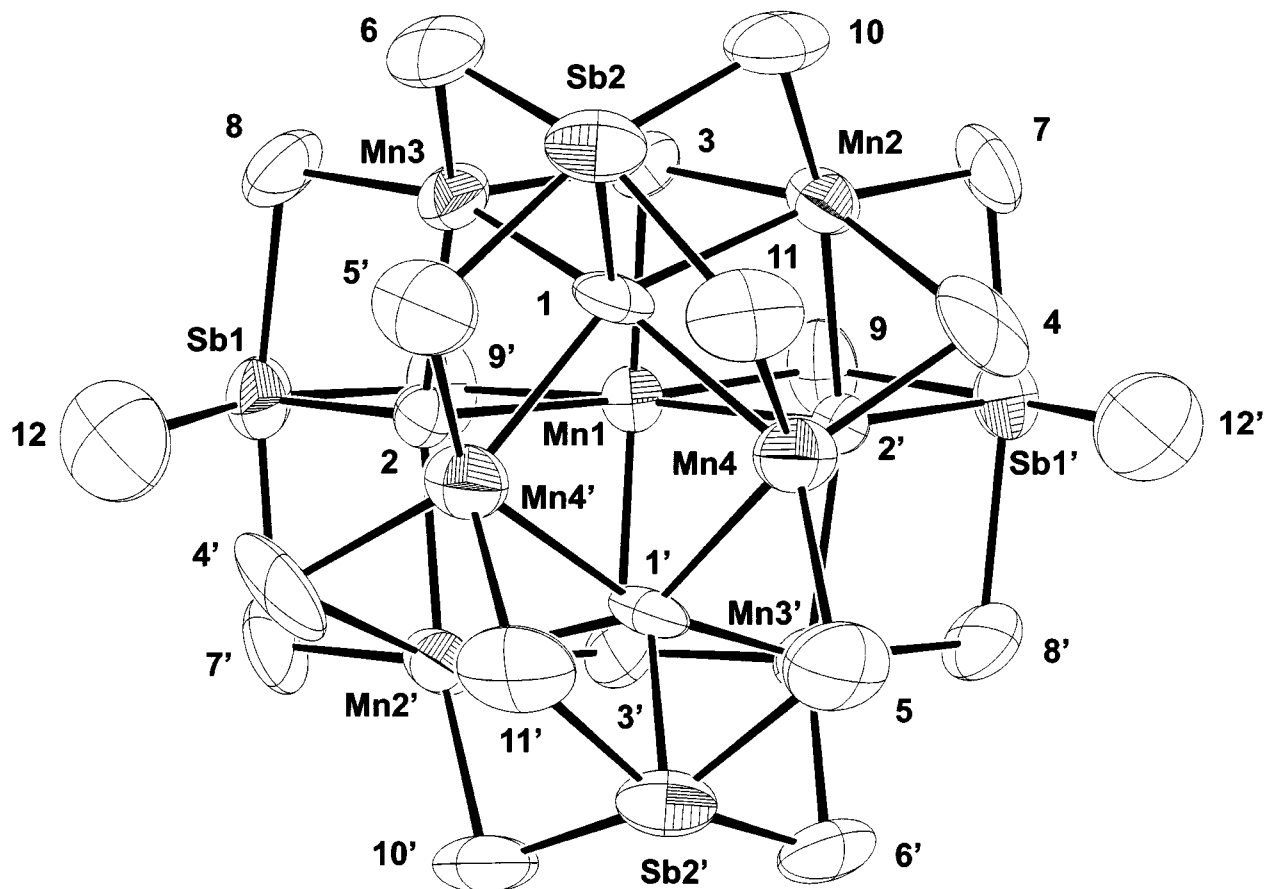
FIG. 2. Labeled ORTEP drawing of the molecular structure of $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$. The thermal ellipsoid sizes correspond to the 60% positional probability surface. The view direction is along the twofold rotation axis through Mn(1). The antimony and manganese atoms are plotted with principal axes and octant shading of the ellipsoids, while the oxygen atoms are plotted as ellipsoids with principal axes only. Oxygen atoms are labeled with numbers only, and primed labels refer to atoms related by the twofold rotation symmetry. The ethoxy groups are omitted for clarity.

respectively. The shortest (< 2 Å) bonds are those opposite the antimony lone-pair region, involving the oxooxygen atoms. The long (2.53 Å) bond distance from Sb(1) to the terminal ethanol oxygen O(12) is probably affected by an intramolecular hydrogen bond.

The seven manganese atoms in the molecule have two different kinds of coordinations. Three of the manganese atoms, Mn(1), Mn(2), and Mn(2′), are six-coordinated, while the other four manganese atoms, Mn(3), Mn(4), Mn(3′), and Mn(4′), are five-coordinated. The Mn(1) and Mn(2) atoms are approximately octahedrally coordinated, with average bond distances of 2.22 (6) and 2.22(13) Å and with *bvs* values of 1.9 and 2.0 respectively. The axis of the twofold rotation symmetry goes through the Mn(1) atom at the special position $(0, 1/2, z)$. The five-coordinated manganese atoms Mn(3) and Mn(4) (and Mn(3′) and Mn(4′)) have average bond distances of 2.13(9) and 2.14(7) Å. Two of them, Mn(4) and Mn(4′) have a common coordination edge, giving a short nonbonding Mn(4)$\cdots$Mn(4′) distance of 2.92(4) Å.

The coordination polyhedra of the five-coordinated manganese atoms can be considered distorted square pyramids, where the two square base planes, defined by O(1), O(2), O(6), and O(8) for Mn(3) and O(1), O(1′), O(5), and O(11) for Mn(4), are coplanar with 0.2 Å. The manganese atoms, Mn(3) and Mn(4), are displaced 0.37(1) and 0.75(1) Å above the base planes. The distortion angles between the normal of the oxygen plane and the apical oxygen atom are 16° and 22°, respectively. Five-coordinations can sometimes be described as a linear Berry rearrangement, which describes the transformation from a trigonal bipyramid (D_{3h}) to a square pyramid (C_{4v}) geometry (20, 21). However, in the present case the five-coordinated atoms are part of a molecule and subject to large intrinsic geometrical constraints. The most proper description of the five-coordinated manganese atoms will probably be as distorted square pyramids.

The five-coordinated oxooxygen atom O(1) can be considered as having a coordination polyhedra of a distorted
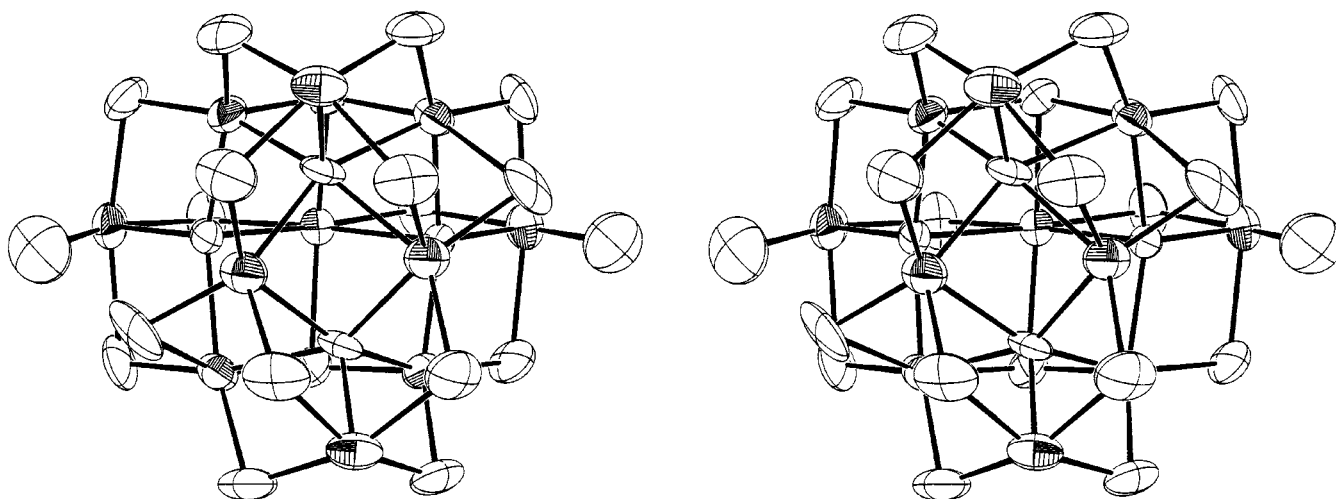
FIG. 3. ORTEP stereo drawing of the molecular structure of $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$, with the same orientation as Fig. 2.

square pyramid, while the other oxooxygen, the four-coordinated O(2) and O(2′), can be considered as being tetrahedrally coordinated. The remaining oxygen atoms are $\mu_3[O(3)]$ and μ [O(4)–O(11)], respectively. The O(12) is terminal and belongs to the only ethanol group present in the molecule. O(12) is involved in an intramolecular hydrogen bond to O(4) with a short hydrogen bond distance observed to be 2.31(3) Å. The lower limit for a short hydrogen bond is about 2.38 Å (22). The explanation for the observed distance of 2.31 Å is probably shortening due to thermal motion. The two oxygen atoms involved both exhibit very large thermal motions (see Fig. 2).

The anisotropic thermal vibrational parameters have been analyzed in terms of a rigid-body thermal analysis according to the technique described by Hirschfeld (23) and Rosenfield et al. (24). The analysis was performed on the metal–oxygen core structure excluding terminal oxygen atoms.

A preliminary analysis of the parameters describing the anisotropic thermal vibrations of the atoms revealed that the two oxygen atoms, O(4) and the terminal O(12), involved in the intramolecular hydrogen bond, did not follow the pattern of the rest of the atoms. As they are involved in an hydrogen bond, these two oxygen atoms can be assumed to exhibit a constrained thermal motion and were therefore excluded from the analysis. The calculations were performed with the program THMA11 (25). The average difference between the mean-square thermal displacement amplitudes along the interatomic distances is 0.0091 Å^2, and the weighted R value between the reproduced and observed thermal parameters was calculated to be 0.085, using e.s.d.'s as atomic weights. The agreement between observed and predicted parameters gives some support for the assumed rigidity of the metal–oxygen core fragment of $Mn_7Sb_4O_4(OEt)_{18}(HOEt)_2$.

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