

## Synthesis and Structural Investigation of a New Bimetallic Alkoxide with the Composition $\text{Mg}_2\text{Sb}_4(\text{OC}_2\text{H}_5)_{16}$

U. BEMM, K. LASHGARI, R. NORRESTAM,\* M. NYGREN,  
AND G. WESTIN

*Departments of Inorganic and Structural Chemistry, Arrhenius Laboratory,  
Stockholm University, S-10691 Stockholm, Sweden*

Received June 15, 1992; accepted September 11, 1992

The new bimetallic antimony alkoxide  $\text{Mg}_2\text{Sb}_4(\mu_3\text{-OEt})_2(\mu\text{-OEt})_8(\text{OEt})_6$  has been prepared by reacting  $\text{Mg}(\text{OEt})_2$  with an excess of  $\text{Sb}(\text{OEt})_3$  in a toluene-ethanol solution, and its molecular structure has been established by single crystal X-ray diffraction techniques. The compound crystallizes with the triclinic space group symmetry  $P\bar{1}$ . The unit cell, which contains one formula unit, has the dimensions  $a = 9.128(4)$ ,  $b = 12.168(4)$ ,  $c = 12.640(6)$  Å,  $\alpha = 64.06(2)^\circ$ ,  $\beta = 79.96(2)^\circ$ , and  $\gamma = 87.29(2)^\circ$ . The derived structural model has been refined against the 3235 most significant observed X-ray reflections, collected at 170(2) K, to an  $R$ -value of 0.030. The molecular structure has a major fragment similar to that found in tetrameric alkoxides or bimetallic alkoxides with the compositions  $M_4(\text{OR})_m$  and  $M_2M'_2(\text{OR})_n$ , respectively. The metal-oxygen skeleton of the fragment forms a rather rigid unit, as judged by an analysis of the determined thermal displacement parameters. The  $\text{Mg}^{2+}$  ions are octahedrally coordinated by the ethoxy oxygen atoms and the  $\text{Sb}^{3+}$  ions can be considered to have a trigonal bipyramidal coordination when the four ethoxy oxygen atoms and the lone pair are taken into account. Extended Hückel calculations verify that the  $\text{Mg-O}$  bonds are rather ionic, while the shorter  $\text{Sb-O}$  bond are more covalent. © 1993 Academic Press, Inc.

### Introduction

In recent years heterometallic alkoxide complexes have attracted interest as potential precursors in the preparation of multi-component oxide-based electroceramics and catalysts via sol-gel techniques. To understand the special properties of such alkoxides, the knowledge of the molecular structures of the compounds formed and their structural relations are of crucial importance.

However, the number of reliable struc-

tural investigations carried out on heterometallic alkoxide complexes is limited, especially for bimetallic alkoxides as is obvious from recent reviews (1). Frequently, relatively complicated types of molecular species are found for these alkoxides. The molecular complexities imply that a fair amount of structural information is needed before any reliable general conclusions can be drawn about the structural chemistry and about the structure-function relationship of bimetallic alkoxides. As regards antimony containing alkoxide complexes, only three previous structural investigations (2-4) have been performed. These

\* To whom correspondence should be addressed.

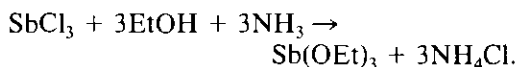
investigations, which concern divalent transition metal–Sb<sup>3+</sup> alkoxides, viz. Ni<sub>5</sub>Sb<sub>3</sub>O<sub>2</sub>(OEt)<sub>15</sub>(HOEt)<sub>4</sub>, Ni<sub>6</sub>Sb<sub>4</sub>O<sub>4</sub>(OEt)<sub>16</sub>(HOEt)<sub>4</sub>, and Mn<sub>8</sub>Sb<sub>4</sub>O<sub>4</sub>(OEt)<sub>20</sub>, showed that the three different compounds contained 8–12 metal ions in each molecule. Apart from the presence of two different metal ions, the complexities of the three molecular entities are also governed by the presence of oxide ions bonded to the Sb<sup>3+</sup> ions and possible hydrogen bonds.

The present study describes a structural investigation of the first alkaline earth metal–antimony alkoxide, Mg<sub>2</sub>Sb<sub>4</sub>(OEt)<sub>16</sub>. Together with the three studies cited above, the investigation is a part of a research program on heterometallic alkoxides. In its present state, the research program is particularly focused on complexes containing trivalent antimony.

## Experimental

### Preparation

All preparations and manipulations of crystals were performed in a glove box with dry (<1 ppm) oxygen free (<1 ppm) nitrogen atmosphere. Mg(OEt)<sub>2</sub>, used as a precursor, was prepared by dissolving polished magnesium metal in an ethanol–toluene (1:2 by volume) solution containing small amounts of iodine. The Mg(OEt)<sub>2</sub> formed was then washed with ethanol to remove the iodine, followed by evaporation to dryness in vacuum. The antimony ethoxide precursor was prepared by adding SbCl<sub>3</sub> to a two phase mixture of hexane and ethanol in the presence of dry distilled NH<sub>3</sub> gas, according to the reaction



The ethanol phase with the precipitated NH<sub>4</sub>Cl was separated from the hexane phase containing the formed Sb(OEt)<sub>3</sub>. By evaporation of the hexane, the obtained

crude Sb(OEt)<sub>3</sub> was finally distilled in vacuum (76–80°C under 0.3 Torr). The toluene and ethanol used were dried with Na and 3 Å molecular sieves, respectively, and saturated with nitrogen.

0.135 g (1.18 mmol) of Mg(OEt)<sub>2</sub> was added to 12.5 ml of a toluene–ethanol (4:1 by volume) solution. After adding 1.52 g (5.92 mmol) of liquid Sb(OEt)<sub>3</sub>, Mg(OEt)<sub>2</sub> slowly dissolved. The solubility of the metal–antimony alkoxide can be decreased by increasing the amount of ethanol in the solvent. During the subsequent stepwise evaporation of the solution, the ethanol content was increased by adding small amounts of a more ethanol-rich toluene–ethanol solution. The crystals start to grow after evaporation of approximately 80% of the toluene–ethanol solution.

### Structural Investigation

A few selected colorless crystals, prepared as above, were put into glass capillaries, which were sealed. The crystal finally selected for data collection was studied using a STOE 4-circle diffractometer using graphite monochromatized MoK $\alpha$  radiation. The diffractometer was equipped with a nitrogen gas stream cryostat set to cool the crystal down to 170 K. From the symmetry observed among the intensities of a preliminary X-ray diffraction data set, and from a determination of the unit cell parameters using the  $\theta$ -values of a limited set of well centered reflection positions, the space group symmetry was deduced to be triclinic with the unit cell parameters  $a = 9.128(4)$ ,  $b = 12.168(4)$ ,  $c = 12.640(6)$  Å,  $\alpha = 64.06(2)^\circ$ ,  $\beta = 79.96(2)^\circ$ , and  $\gamma = 87.29(2)^\circ$ . Single crystal X-ray diffraction data at 170 K were collected from the selected crystal and corrected for background, Lorentz polarization, and absorption effects (cf. Table I). The minor absorption from the glass capillary (wall thickness 0.01 mm) was neglected. Intensity statistics indicated the electron distribution in the unit cell to be

TABLE I  
EXPERIMENTAL CONDITIONS FOR THE CRYSTAL STRUCTURE  
DETERMINATION OF  $\text{Mg}_2\text{Sb}_4(\text{OC}_2\text{H}_5)_{16}$

Formula (X-ray study)	$\text{Mg}_2\text{Sb}_4(\text{OC}_2\text{H}_5)_{16}$
Formula weight	1256.6 g/mol
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.128(4)$ , $b = 12.168(4)$ , $c = 12.640(6)$ Å $\alpha = 64.06(2)^\circ$ , $\beta = 79.96(2)^\circ$ , $\gamma = 87.29(2)^\circ$
Unit cell volume, $V$	1243(1) Å <sup>3</sup>
Formula units per unit cell, $Z$	1
Calculated density, $D_x$	1.679(1) g. cm <sup>-3</sup>
Radiation	MoK $\alpha$
Wavelength, $\lambda$	0.71073 Å
Temperature, $T$	170(2) K
Crystal shape	Prismatic
Crystal size	0.49 × 0.22 × 0.17 mm <sup>3</sup>
Diffractometer	Stoe 4-circle
Determination of unit cell:	
Number of reflections used	16
$\theta$ -range	10.3°–15.0°
Intensity data collection:	
Maximum $\sin(\theta)/\lambda$	0.54 Å <sup>-1</sup>
Range of $h$ , $k$ , and $l$	–9 to 9, –13 to 13, and 0 to –13
Standard reflections	3
Intensity instability	3%
Internal $R$	0.015
Number of collected reflections	3492
Number of unique reflections	3235
Number of observed reflections	2545 (79%)
Criterion for significance	$I > 5 \cdot \sigma(I)$
Absorption correction:	
Linear absorption coefficient	Numerical integration 22.4 cm <sup>-1</sup>
Transmission factor range	0.70–0.74
Structure refinement:	
Minimization of	Fullmatrix least squares $\Sigma w \cdot \Delta F^2$
Anisotropic thermal parameters	Metal, C and O
Isotropic thermal parameters	H
Number of refined parameters	368 (with 72 constraints)
Weighting scheme	$(\sigma^2(F) + 0.0002 F ^2)^{-1}$
Final $R$ for observed refls.	0.030
Final $wR$ for observed refls.	0.045
Final $wR$ for all 3235 refls.	0.050
Final $(\Delta/\sigma)_{\text{max}}$ (nonhydrogen)	0.3
Final $\Delta\rho_{\text{min}}$ and $\Delta\rho_{\text{max}}$	–0.8 and +0.5 e <sup>-</sup> /Å <sup>3</sup>

centric and accordingly  $P\bar{1}$  was chosen as the probable space group. The choice of  $P\bar{1}$  as the correct space group is further supported by the outcome of the structural refinement.

The Mg:Sb ratio of about 1:2, obtained from the energy dispersive X-ray spectra for a hydrolyzed alkoxide specimen, collected with a scanning electron microscope (JEOL 820, LINK AN10000), together with rough

estimates of expected possible molecular volumes suggest that the metal ion content in the unit cell would be two magnesium and four antimony atoms. Preliminary positions of the antimony atoms were derived from interpretation of a calculated Patterson function. The positions of the remaining nonhydrogen atoms were obtained from subsequent least squares refinements and difference electron density ( $\Delta\rho$ ) calculations. The hydrogen atom positions of the ethoxy groups were initially derived by assuming ideal geometries of the methylene and methyl groups. The methyl hydrogen positions were then refined by allowing the hydrogens to rotate as rigid groups around the C–C bonds. In the final refinement stages the positions of the hydrogens were allowed to vary, under the constraints that all methylene and methyl hydrogens had common atomic displacement (thermal) parameters, carbon–hydrogen bond lengths, and hydrogen–hydrogen distances. The obtained isotropic displacement parameters of 0.028(5) and 0.036(5) Å<sup>2</sup> and the carbon–hydrogen bond length of 1.00(2) Å and hydrogen–hydrogen distance of 1.62(3) Å for the methylene and methyl hydrogen atoms indicate the obtained hydrogen parameters to be physically reasonable. The coordinates and thermal parameters obtained in the final structural refinement ( $R = 0.030$ ) are listed in Table II and selected bond distances and angles in Table III. The labeling scheme used, together with the obtained molecular conformation, is shown in Fig. 1. The methylene and methyl carbon atoms of the ethoxy groups are labeled with the same number as that of the oxygen atom followed by A and B, respectively.

Further details on the experimental conditions and the final structural refinement are given in Table I. Most of the crystallographic calculations were performed using SHELX-76 (5) and PLATON (6) computer programs. The calculations concerning in-

TABLE II  
THE FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ )  
AND THERMAL PARAMETERS ( $\times 10^3$ ) WITH E.S.D.'S,  
FOR THE NONHYDROGEN ATOMS OF  $\text{Mg}_2\text{Sb}_4(\text{OEt})_{16}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Sb(1)	1699(1)	2001(1)	−2105(1)	21.5(2)
Sb(2)	−589(1)	2812(1)	1959(1)	27.2(2)
Mg	−307(3)	901(2)	679(2)	19(1)
O(1)	−472(5)	877(4)	−978(4)	21(2)
O(2)	1674(6)	1819(4)	−459(4)	23(2)
O(3)	−2119(5)	−262(4)	1734(4)	24(2)
O(4)	−1207(6)	2498(4)	498(4)	25(2)
O(5)	83(6)	1111(4)	2187(4)	24(2)
O(6)	3887(6)	2395(5)	−2449(4)	26(2)
O(7)	−379(6)	2375(5)	3677(5)	43(2)
O(8)	−2717(6)	2527(5)	2526(5)	43(2)
C(1A)	−1701(9)	1442(7)	−1580(6)	26(3)
C(1B)	−3164(10)	865(8)	−916(8)	38(3)
C(2A)	2773(9)	2445(7)	−202(7)	27(3)
C(2B)	2647(11)	3810(8)	−769(9)	47(4)
C(3A)	−3513(8)	84(7)	2250(7)	25(3)
C(3B)	−3679(10)	−363(9)	3584(8)	42(4)
C(4A)	−1542(9)	3604(7)	−425(7)	29(3)
C(4B)	−3193(11)	3735(9)	−447(9)	51(4)
C(5A)	336(9)	181(7)	3335(7)	28(3)
C(5B)	1942(11)	163(9)	3464(9)	51(4)
C(6A)	4456(13)	3356(13)	−3536(9)	70(5)
C(6B)	5991(15)	3655(16)	−3720(12)	92(7)
C(7A)	776(11)	2961(9)	3858(9)	55(4)
C(7B)	213(15)	3841(12)	4346(13)	99(7)
C(8A)	−3524(10)	2787(9)	3446(8)	46(4)
C(8B)	−5077(11)	3069(9)	3230(8)	50(4)

tensity statistics and absorption effects were carried out using two programs, ENORM and STOEABS, written by one of the authors (R.N.). Atomic scattering factors with anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography (7).

## Discussion

The molecular formula of the present magnesium antimony ethoxide can be written as  $\text{Mg}_2\text{Sb}_4(\mu_3\text{-OEt})_2(\mu\text{-OEt})_8(\text{OEt})_6$  as seen in Fig. 1. The unit cell contains only

TABLE III  
 BOND DISTANCES (Å) AND ANGLES (°) WITH E.S.D.'S BETWEEN THE  
 NONHYDROGEN ATOMS IN  $Mg_2Sb_4(OEt)_{16}$ —PRIMED ATOMS ARE ATOMS  
 GENERATED THROUGH THE INVERSION CENTER

Sb(1)–O(1)	2.323(5) Å	Mg–O(1)	2.139(6) Å
–O(2)	1.990(5)	–O(1')	2.136(5)
–O(3')	1.990(5)	–O(2)	2.113(6)
–O(6)	2.003(6)	–O(3)	2.078(6)
Sb(2)–O(4)	2.208(5)	–O(4)	2.007(6)
–O(5)	2.040(5)	–O(5)	2.120(5)
–O(7)	2.040(5)		
–O(8)	1.941(6)		
O(1)–C(1A)	1.441(9)	C(1A)–C(1B)	1.471(12)
O(2)–C(2A)	1.448(10)	C(2A)–C(2B)	1.502(14)
O(3)–C(3A)	1.457(10)	C(3A)–C(3B)	1.510(12)
O(4)–C(4A)	1.406(10)	C(4A)–C(4B)	1.511(14)
O(5)–C(5A)	1.447(9)	C(5A)–C(5B)	1.501(13)
O(6)–C(6A)	1.389(13)	C(6A)–C(6B)	1.418(19)
O(7)–C(7A)	1.404(12)	C(7A)–C(7B)	1.485(20)
O(8)–C(8A)	1.413(12)	C(8A)–C(8B)	1.486(14)
O(1)–Sb(1)–O(2)	74.6(2)°	O(4)–Sb(2)–O(5)	72.5(2)°
O(1)–Sb(1)–O(3')	73.5(2)	O(4)–Sb(2)–O(7)	156.0(2)
O(1)–Sb(1)–O(6)	154.6(2)	O(4)–Sb(2)–O(8)	81.1(2)
O(2)–Sb(1)–O(3')	95.8(2)	O(5)–Sb(2)–O(7)	89.7(2)
O(2)–Sb(1)–O(6)	88.2(2)	O(5)–Sb(2)–O(8)	101.7(2)
O(3')–Sb(1)–O(6)	90.1(2)	O(7)–Sb(2)–O(8)	87.0(2)
O(1)–Mg–O(1')	78.8(2)	Sb(1)–O(1)–Mg	98.2(2)
O(1)–Mg–O(2)	76.3(2)	Sb(1)–O(1)–Mg'	98.3(2)
O(1')–Mg–O(2)	94.3(2)	Sb(1)–O(2)–Mg	110.7(3)
O(1)–Mg–O(3)	98.3(2)	Sb(1')–O(3)–Mg	112.1(3)
O(1')–Mg–O(3)	76.0(2)	Sb(2)–O(4)–Mg	104.9(2)
O(1)–Mg–O(4)	102.6(2)	Sb(2)–O(5)–Mg	106.9(2)
O(1')–Mg–O(4)	174.9(2)	Mg–O(1)–Mg'	101.2(2)
O(1)–Mg–O(5)	172.3(2)	O(1)–C(1A)–C(1B)	114.2(6)
O(1')–Mg–O(5)	104.2(2)	O(2)–C(2A)–C(2B)	113.2(7)
O(2)–Mg–O(3)	169.8(3)	O(3)–C(3A)–C(3B)	113.0(7)
O(2)–Mg–O(4)	90.9(2)	O(4)–C(4A)–C(4B)	112.7(7)
O(2)–Mg–O(5)	96.3(2)	O(5)–C(5A)–C(5B)	111.7(7)
O(3)–Mg–O(4)	98.9(2)	O(6)–C(6A)–C(6B)	116.1(10)
O(3)–Mg–O(5)	89.4(2)	O(7)–C(7A)–C(7B)	112.3(9)
O(4)–Mg–O(5)	75.0(2)	O(8)–C(8A)–C(8B)	109.1(8)

one molecule and thus the space group symmetry constrains the molecule to have inversion ( $C_i$ ) symmetry. Excluding the terminal ethoxy groups bonded to the antimony atoms Sb(2) and Sb(2'), the molecular symmetry (cf. Fig. 1) can be approximately described as  $C_{2h}$ . Excluding Sb(2) and Sb(2')

and the terminal ethoxy groups attached to them (cf. Fig. 1), the obtained structural entity is similar to that frequently found in tetrameric alkoxides, e.g.,  $Ti_4(OEt)_{16}$  (8) and  $W_4(OEt)_{16}$  (9), and in some bimetallic alkoxides with the metal composition  $M_2M'_2$  (1).

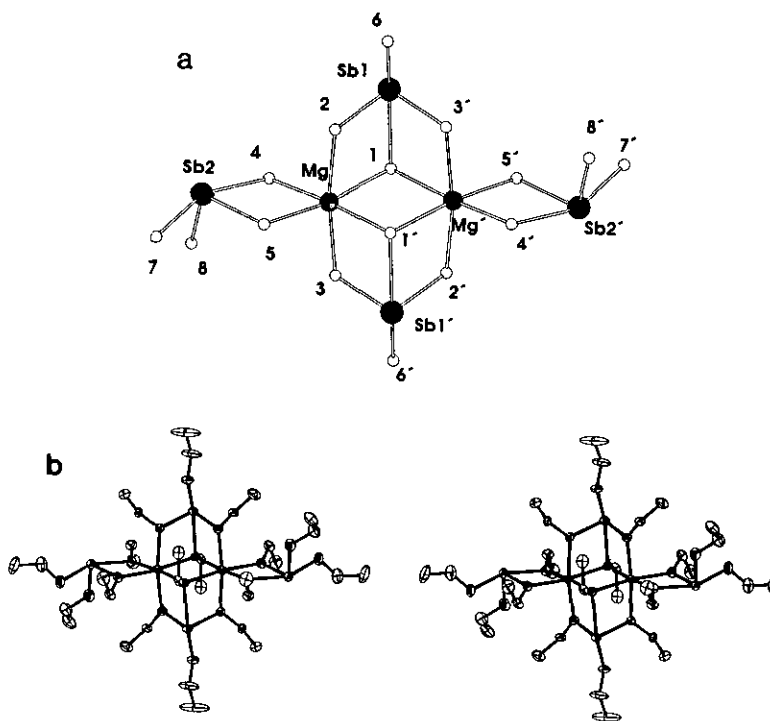


FIG. 1. (a) The atomic numbering scheme used in the present study of  $\text{Mg}_2\text{Sb}_4(\text{OEt})_{16}$ . Unprimed atoms represent atoms in the asymmetric unit, and primed atoms are those generated by the crystallographic inversion center. For clarity only metal and oxygen atoms are included. (b) Stereo drawing of the molecular conformation of  $\text{Mg}_2\text{Sb}_4(\text{OEt})_{16}$ . The probability ellipsoids of the atomic positions, calculated from the anisotropic thermal parameters, are drawn at the 50% probability level. Hydrogen atoms are omitted.

The two symmetry independent antimony atoms are both coordinated by four oxygen atoms with three Sb–O distances in the range 1.94–2.04 Å and the fourth distance considerably longer (2.322(5) and 2.208(5) Å). Calculations of empirical bond valence sums (bvs) for the antimony atoms, using the parameters given by Brown and Altermatt (10), verify that the bond distance distributions agree with those commonly found for trivalent antimony ions (bvs-values slightly above 3). By taking into account the expected location of the lone pair region of  $\text{Sb}^{3+}$ , the coordination geometry can be regarded as a distorted trigonal bipyramid. As shown in Fig. 2, distortion from bipyra-

midal arrangement around each antimony atom is evident for the axial oxygen atom involved in the long Sb–O bond. From the observed axial O–Sb–O angles at Sb(1) and Sb(2), the angular distortions  $\alpha$  (cf. Fig. 2) are 25.4° and 24.0°. The equatorial O–Sb–O angles are, as usual, considerably smaller (95.8° and 101.6°) than the ideal trigonal value of 120°, while the O–Sb–O angles between the short axial Sb–O bond and the two equatorial Sb–O bonds are close to 90°. The bond length and bond angle distributions observed around the four-coordinated antimony atom in the Ni–Sb alkoxide,  $\text{Ni}_5\text{Sb}_3\text{O}_2(\text{OEt})_{15}(\text{HOEt})_4$  (2), agree well with those found in the present compound.

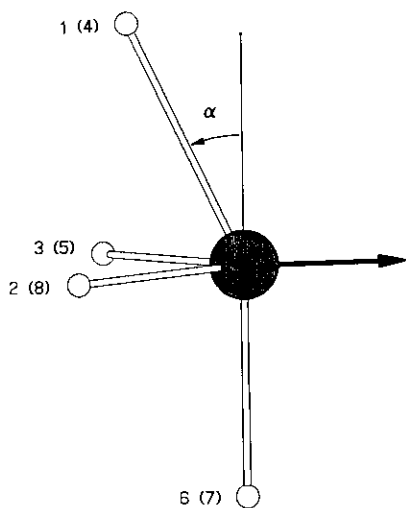


FIG. 2. The coordination geometry around the Sb atoms (dark grey) in  $\text{Mg}_2\text{Sb}_4(\text{OEt})_{16}$ . The numbers given are the labels (cf. Table I) for the oxygen atoms around the Sb(1) atom and in parentheses the labels of the oxygens around the Sb(2) atom. The axial distortion  $\alpha$  observed for the long Sb–O bonds is also indicated. The thick horizontal arrow is pointing into the expected lone pair region of the  $\text{Sb}^{3+}$  ions.

Each magnesium atom is coordinated to six ethoxy oxygen atoms to form a slightly distorted octahedron. The  $bvs$ -value estimated for the bond length distribution around Mg is 2.0, in agreement with the formal valence. The Mg–O bond of 2.007 Å formed to the  $\mu$ -oxygen O(4) is shorter than the other Mg–O bonds. It should be noted that the  $\mu$ -oxygen O(4) atom forms a long bond, 2.208 Å, to one of the antimony atoms (cf. above).

The distortions of the oxygen coordination polyhedra around the metal ions, as reflected by the deviations in the oxygen–metal–oxygen bond angles, can be qualitatively interpreted by the well-known "rules" for distortions (see, e.g., (11)) of coordination geometry that occur when two metal ions share a common coordination edge. Thus, the bond angles at the metal ions that involve the edge-forming oxygen

atoms are substantially reduced due to metal–metal repulsion. Accordingly, such bond angles in the present structure range from 72.5° to 78.8°. The lower values are encountered at the  $\text{Sb}^{3+}$  atoms and the higher values when the metal ions involved are both  $\text{Mg}^{2+}$ . From Fig. 1 it is seen that the coordination polyhedra around the metal atoms Sb(2), Mg, Mg', and Sb(2') are linked by edge-sharing. A least-squares plane through the four metal and six oxygen atoms involved shows the atoms to be coplanar within 0.16 Å.

The atoms O(6), Sb(1), O(1), O(1'), Sb(1'), and O(6') are coplanar within 0.04 Å and thus result in the core having approximate  $C_{2h}$  symmetry. As shown in Fig. 1, the carbon atoms of the ethyl groups attached to these oxygen atoms are almost aligned with the  $C_{2h}$  mirror plane. Planes through the  $\alpha$ -carbon atoms and the two metal ions bonded to each of the  $\mu$ -oxygen atoms O(2), O(3), O(4), and O(5) show these oxygens to deviate by less than 0.22 Å. It should be noted that the position of the six metal atoms in the molecule are coplanar within 0.07 Å.

From Table II it is seen that the carbon atoms C(6a), C(6b), and C(7b), all belonging to terminal ethoxy groups, have large thermal vibration amplitudes. The anisotropic thermal parameters show that the vibration of C(7b) is rather isotropic, but those of the C(6a) and C(6b) atoms are highly anisotropic (large  $U_{22}$  components) indicating a possible positional disorder (mainly along  $y$ ) of the latter two carbon atoms. No indication of alternative partially occupied positions for the C(6a) and C(6b) atoms that would suggest a more substantial disorder was found in  $\Delta\rho$  maps. Anyhow, the geometry of the ethoxy group number 6 must be regarded as being of limited physical relevance. The  $\text{O}-\text{C}_\alpha-\text{C}_\beta$  bond angles (109 to 114°), the  $\text{O}-\text{C}_\alpha$  bond lengths (1.41 to 1.46 Å), and the  $\text{C}_\alpha-\text{C}_\beta$  bond lengths (1.47 to 1.51 Å) of the remaining ethoxy groups are all close to standard values. The methyl groups have

staggered conformations, as the largest value of the  $O-C_\alpha-C_\beta-H$  torsion angles in each methyl group is close to  $180^\circ$  ( $172$  to  $184^\circ$ ). The bvs-values of the oxygen atoms are all close to 2 (1.8 to 2.1). The rather constant values of the oxygen bvs-values also reflects that, in general, the metal-oxygen distances decrease for the  $\mu_3$ ,  $\mu$ , and terminal oxygens, respectively.

The anisotropic thermal parameters were analyzed for the presence of any major rigid group of atoms in the molecule, using the tests described by Hirshfeld (12) and Rosenfield *et al.* (13). These tests indicated that a major central fragment, consisting of 14 metal and oxygen atoms, was possibly vibrating as a rigid group. The differences between the thermal mean square displacement amplitudes along interatomic directions in the indicated rigid group were all less than  $0.004 \text{ \AA}^2$ . The 14-atom rigid group consists of the central metal and oxygen atoms that remain after omitting the terminal  $O(7)-Sb(2)-O(8)$  groups and the terminal  $O(6)$  atoms. The computer program THMA11 (14) was used to estimate the 12 independent parameters of the two symmetric matrices describing the translation and libration motions of the atoms in the rigid fragment. With these parameters, the observed anisotropic thermal parameters are predicted within two e.s.d.'s. The close agreement between observed and predicted anisotropic parameters (weighted  $R$ -value of 0.046) further supports the assumed rigidity of the central molecular fragment. The corrections to the bond distances due to rigid body motion are negligible ( $<0.0011 \text{ \AA}$ ).

To gain more information on the charge and bond order distribution within the  $Mg_2Sb_4(OC_2H_5)_{16}$  molecule, semiempirical molecular orbital calculations of the extended Hückel type (15, 16) were performed for the observed molecular geometry using the parameters compiled by Alvarez (17). To check the relevance of the method when

applied to metal alkoxides, a calculation was performed on the  $Al_2(OH)_6$  molecule and compared with the more rigorous ab initio calculations on this molecule that were published recently (18). The atomic charges, estimated as gross atomic populations from the obtained extended Hückel orbitals, became +2.0 and  $-1.1$  for the Al and O atoms, respectively. These charges agree well with those (+2.05 and about  $-1.15$ ) obtained from the ab initio calculations. To reduce the number of orbitals needed for the calculations on the present  $Mg_2Sb_4(OC_2H_5)_{16}$  molecule, all ethoxy groups were replaced by methoxy groups having ideal geometries. The estimated atomic charges became +1.6 for both the Sb and Mg atoms and ranged from  $-1.1$  to  $-0.9$  for the oxygen atoms, with the lowest value ( $-1.1$ ) obtained for the  $\mu_3$ -oxygen O(1). The overlap populations of all the Mg-O bonds and of the longer Sb-O bonds (Sb(1)-O(1) and Sb(2)-O(4)) are about 0.1. The remaining shorter Sb-O bonds, three at each Sb atoms, have populations ranging from 0.3 to 0.5, indicating less ionic character in these bonds. These more covalent Sb-O bonds are those forming the O-Sb-O angles of about  $90^\circ$ .

### Acknowledgments

The research on bimetallic alkoxides is financially supported by the Swedish Natural Science Research Council.

### References

1. K. G. CAULTON AND L. G. HUBERT-PFALZGRAF, *Chem. Rev.* **90**, 965-995 (1990).
2. U. BEMM, R. NORRESTAM, M. NYGREN, AND G. WESTIN, *Inorg. Chem.*, in press. (1992).
3. U. BEMM, R. NORRESTAM, M. NYGREN, AND G. WESTIN, submitted for publication.
4. U. BEMM, R. NORRESTAM, M. NYGREN, AND G. WESTIN, to be published.
5. G. M. SHELDRIK, "SHELX76, Program for crystal structure determination," Univ. of Cambridge, 1976.
6. A. L. SPEK, "PLATON, Program for the analysis of molecular geometry," Univ. of Utrecht, 1988-1990.



7. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch, Birmingham, 1974.
8. J. A. IBERS, *Nature* **197**, 686 (1963).
9. M. H. CHISHOLM, J. C. HUFFMAN, C. C. KIRKPATRICK, J. LEONELLI, AND K. FOLTING, *J. Am. Chem. Soc.* **103**, 6093-6099, 1985.
10. I. D. BROWN AND D. ALTERMATT, *Acta Crystallogr. Sect. B* **41**, 244-247 (1985).
11. L. PAULING, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, New York, 1960.
12. F. L. HIRSHFELD, *Acta Crystallogr. Sect. A* **32**, 239 (1976).
13. R. E. ROSENFELD, JR., K. N. TRUEBLOOD, AND J. D. DUNITZ, *Acta Crystallogr. Sect. A* **34**, 828 (1978).
14. K. N. TRUEBLOOD, *Acta Crystallogr. Sect. A* **34**, 950 (1978).
15. R. HOFFMAN, *J. Chem. Phys.* **39**, 1397 (1963).
16. M.-H. WHANGBO, M. EVAIN, T. HUGHBANKS, M. KERTESZ, S. WIJESEKERA, C. WILKER, C. ZHENG, AND R. HOFFMAN, "EHMACC. Program for extended Hückel molecular and crystal calculations," Cornell Univ., Ithaca, NY, 1976-1987.
17. S. ALVAREZ, "Collected Tables for Extended Hückel Calculations," Univ. de Barcelona, 1989.
18. R. H. CAYTON, M. H. CHISHOLM, E. R. DAVIDSON, V. F. DiSTASI, P. DU, AND J. C. HUFFMAN, *Inorg. Chem.*, 1020 (1991).