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Contribution from the Departments of Structural and Inorganic Chemistry,
Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden

Synthesis and Molecular Structure of $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$

U. Bemm, R. Norrestam,* M. Nygren, and G. Westin

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A new Ni–Sb alkoxide of the formula $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$ has been prepared by reacting anhydrous $NiCl_2$ with $NaSb(OEt)_4$ and NaOEt in a toluene/ethanol solution in dry, oxygen-free atmosphere. $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$ crystallizes in the noncentrosymmetric space group $Pca2_1$, with $a = 17.909$ (2) Å, $b = 20.608$ (3) Å, $c = 17.221$ (2) Å, $V = 6356$ (1) Å^3, $Z = 4$, $D_x = 1.621$ (4) g/cm^3, and fw = 1550.89. The crystal structure was refined to $R = 0.041$ ($R_w = 0.050$) for the 3049 most significant single-crystal X-ray diffraction intensities collected with Mo Kα radiation (λ(Mo Kα) = 0.7107 Å, μ(Mo Kα) = 27.8 cm^{-1}) at room temperature ($T = 293$ (1) K). The packing of the wedge-shaped molecules can be considered as body-centered cubic. One of the Sb atoms is four-coordinated by the oxygen atoms, while the other two are five-coordinated. The Sb atoms are all trivalent, and the stereoactive lone pairs complete the coordinations. Thus, the coordinations around the Sb atoms become distorted trigonal-bipyramidal and octahedral, respectively. Three of the five Ni atoms are approximately octahedrally coordinated by oxygen atoms, and the remaining two Ni atoms five-coordinated in the shape of a distorted square pyramid.

Introduction

The use of alkoxides as precursors in sol-gel processing of ceramic materials has led to an increasing interest in preparation of bimetallic alkoxides, but reliable information based on the molecular structures is limited to a few cases.

However, during the last few years the structures of a few bimetallic alkoxides have been solved by single-crystal X-ray diffraction techniques. It has shown that the complexes often have complicated molecular structures and even in some cases contain unexpected oxy oxygens.[1] Detailed and extended knowledge of the structures of the alkoxides is obviously of importance for the basic understanding of structural principles within this class of compounds and for more practical applications in connection with sol-gel preparation of new materials. In this article the structure of a new Ni^{2+}–Sb^{3+}-ethoxide is presented. Previously, only two other M^{2+}–Sb^{3+} ethoxides, $Sn_3Sb(OEt)_{11}$ and $SnSb_2(OEt)_8$, have been prepared,[2,3] but their detailed molecular structures are unknown.

The present investigation constitutes one part of an extended research program concerning synthesis and characterization of M^{2+}–Sb^{3+} ethoxides. The possibilities to prepare such complexes with M^{2+} = Cr, Mn, Fe, Co, Ni, Cu, and Zn have recently been described.[4]

Experimental Section

Preparation. All preparations and the manipulation of crystals for the X-ray data collection were performed in a glovebox containing a dry, oxygen-free, nitrogen atmosphere.

The solvents used, toluene and ethanol, were dried with Na and CaH_2, respectively. Commercial anhydrous $NiCl_2$ was used without further purification. $Sb(OEt)_3$ was synthesized by reacting $SbCl_3$ with ammonia gas in hexane and ethanol.[5] Thereafter the crude $Sb(OEt)_3$ was distilled in vacuum. The synthesis was performed in the following way: 0.818 g of Na was dissolved in 17 mL of ethanol and 60 mL of toluene followed by addition of 4.57 g of $Sb(OEt)_3$. After about 16 h 2.306 g of $NiCl_2$ was added and allowed to react for 5 days, whereby a yellow solution was formed. The NaCl formed during the reaction precipitated.

The residue obtained from a hydrolyzed and dried solution was analyzed in a scanning electron microscope (SEM), equipped for energy dispersive X-ray analysis (EDS), and showed that less than 0.5 mol % NaCl remained. On slow evaporation of the yellow solution, formed as described above, two types of crystals were formed; squarish yellow and green needles.

Table I. Crystallographic Data for $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$

formula	$Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$
fw	1550.89
space group	$Pca2_1$ (No. 29)
unit cell dimens	
a	17.909 (2) Å
b	20.608 (3) Å
c	17.221 (2) Å
unit cell volume, V	6356 (1) Å^3
formula units per unit cell, Z	4
calcd dens, D_x	1.621 (4) g cm^{-3}
wavelength, λ(Mo Kα)	0.71073 Å
temp, T	20 (1) °C
linear abs coeff, μ	27.8 cm^{-1}
transm factor range	0.26–0.37
final R^a for observed refls	0.041
final $R_w{}^b$ for observed refls	0.050

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

Structure Determination. The yellow crystals selected for the present X-ray study were introduced and mounted into glass capillary tubes and sealed within the glovebox. Preliminary investigations of a selected crystal (prismatic 0.5 × 0.5 × 0.5 mm^3) by means of a STOE single-crystal X-ray diffractometer (graphite-monochromatized Mo Kα radiation) indicated primitive orthorhombic space group symmetry. The unit cell parameters were determined and refined from diffractometer determined θ values as $a = 17.909$ (2) Å, $b = 20.608$ (3) Å, and $c = 17.221$ (2) Å.

Single-crystal X-ray diffraction data ((sin Θ)/λ < 0.54 Å^{-1}, 4936 reflections) were collected and corrected for background, Lorentz, polarization, and absorption effects. The possible space groups as indicated by the systematic absences among the X-ray reflections are $Pca2_1$ or $Pcam$. Intensity statistics clearly indicated the noncentrosymmetric space group symmetry $Pca2_1$. The selected symmetry is further supported by the outcome of the investigation. Preliminary Sb positions were obtained by the application of direct methods using the program package SHELXS-86.[6] The remaining atomic positions were found from subsequent calculations of difference electron density ($\Delta\rho$) maps. The origin along the polar z axis was defined by keeping the z coordinate of one of the symmetry-independent Sb atoms fixed to 0. Refining models of the two possible enantiomeric structures yielded R values of 0.041 and 0.045 (R_w = 0.050 and 0.058), respectively. The difference in R (and R_w) secures that the correct enantiomer, used for all subsequent calculations, is the one with the lower R value.

Further details on the experimental conditions and the final structural refinements are given in Table I. The positions of the hydrogen atoms at the methylene and methyl carbon atoms were constrained to geometrically ideal positions (C–H distance 1.00 Å). Least-squares refinements of the structural model yielded a final R value of 0.041. The final atomic coordinates and thermal parameters are listed in Table II.

The structural refinements were carried out by means of the SHELX-76 package,[7] using atomic scattering factors for neutral atoms from ref 8.

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(1) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969–995.

(2) Athar, T.; Bohra, R.; Mehrotra, R. C. *Main Group Met. Chem.* **1987**, *10* (6), 399–410.

(3) Athar, T.; Bohra, R.; Mehrotra, R. C. *Synth. React. Inorg. Met.-Org. Chem.* **1989**, *19* (2), 195–206.

(4) Westin, G.; Nygren, M. *J. Mater. Sci.*, in press.

(5) US Pat. 2 839 554, June 17, 1958; *Chem. Abstr. 53*, **1959**, 1144e.

(6) Sheldrick, G. M. *SHELXS86, Program for direct methods*; University of Cambridge: Cambridge, England, 1986.

(7) Sheldrick, G. M. *SHELX76, Program for crystal structure determination*; University of Cambridge: Cambridge, England, 1976.

(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

0020-1669/92/1331-2050$03.00/0

Table II. Fractional Atomic Coordinates ($\times10^4$) and Thermal Parameters ($\times10^3$), with Esd's, for Non-Hydrogen Atoms of $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$[a]

atom	x	y	z	U_{eq}/U_{iso}, Å^2
Sb(1)	-2400 (1)	2343 (1)	630 (1)	68 (1)
Sb(2)	867 (1)	1058 (1)	0	68 (1)
Sb(3)	38 (1)	3828 (1)	-1566 (1)	53 (1)
Ni(1)	-734 (1)	1706 (1)	216 (2)	57 (1)
Ni(2)	414 (1)	2421 (1)	-818 (2)	49 (1)
Ni(3)	-1126 (1)	3052 (1)	-519 (2)	50 (1)
Ni(4)	1247 (1)	2413 (1)	728 (2)	59 (1)
Ni(5)	887 (1)	3672 (1)	8 (2)	52 (1)
O(1)	-3377 (6)	1981 (7)	256 (8)	90 (6)
O(2)	-1902 (6)	1544 (5)	253 (9)	81 (5)
O(3)	-2258 (5)	2787 (6)	-380 (7)	63 (4)
O(4)	-295 (6)	865 (5)	-174 (8)	74 (5)
O(5)	-711 (5)	2164 (5)	-854 (6)	49 (4)
O(6)	-1080 (5)	3439 (5)	-1598 (7)	55 (4)
O(7)	878 (6)	1533 (5)	-1091 (8)	66 (4)
O(8)	497 (6)	2917 (5)	-1849 (6)	57 (4)
O(9)	-674 (7)	1329 (6)	1370 (8)	85 (5)
O(10)	-1140 (5)	2604 (5)	569 (7)	58 (4)
O(11)	-1412 (6)	3995 (5)	-111 (8)	68 (4)
O(12)	644 (8)	905 (6)	1314 (9)	96 (6)
O(13)	393 (5)	1903 (5)	256 (6)	55 (4)
O(14)	-37 (5)	3363 (4)	-563 (6)	43 (3)
O(15)	-434 (6)	4669 (5)	-807 (7)	64 (4)
O(16)	1805 (6)	1648 (6)	376 (8)	79 (5)
O(17)	1372 (5)	2836 (5)	-320 (6)	49 (4)
O(18)	1085 (6)	4086 (5)	-1007 (7)	55 (4)
O(19)	1054 (7)	2008 (7)	1816 (8)	84 (5)
O(20)	1124 (6)	3306 (6)	1019 (6)	61 (4)
O(21)	372 (6)	4511 (5)	388 (7)	68 (4)
C(1A)	-3999 (15)	2011 (15)	773 (19)	136 (10)
C(1B)	-4648 (25)	1863 (21)	449 (31)	257 (20)
C(2A)	-2263 (14)	904 (11)	301 (15)	113 (8)
C(2B)	-2632 (20)	658 (15)	-338 (22)	182 (13)
C(3A)	-2814 (11)	2772 (10)	-972 (13)	88 (6)
C(3B)	-3360 (18)	3267 (15)	-867 (18)	158 (12)
C(4A)	-527 (17)	197 (13)	-111 (19)	142 (10)
C(4B)	-381 (21)	-239 (16)	-609 (23)	190 (15)
C(5A)	-892 (17)	1796 (15)	-1579 (20)	141 (10)
C(5B)	-1497 (31)	1732 (27)	-1786 (44)	351 (31)
C(6A)	-1619 (13)	3843 (10)	-2019 (14)	96 (7)
C(6B)	-1768 (18)	3622 (13)	-2759 (20)	155 (11)
C(7A)	1453 (16)	1392 (14)	-1628 (19)	144 (10)
C(7B)	1287 (21)	863 (16)	-2162 (23)	195 (15)
C(8A)	556 (13)	2735 (11)	-2613 (15)	100 (7)
C(8B)	1148 (16)	2991 (14)	-3054 (20)	148 (11)
C(9A)	-1153 (23)	1180 (19)	1922 (25)	194 (16)
C(9B)	-952 (27)	1057 (21)	2647 (28)	244 (21)
C(10A)	-720 (9)	2942 (9)	1157 (10)	63 (5)
C(10B)	-1166 (14)	3148 (13)	1855 (16)	122 (9)
C(11A)	-1941 (17)	4285 (14)	259 (20)	155 (11)
C(11B)	-1980 (15)	4881 (12)	598 (19)	137 (9)
C(12A)	794 (16)	254 (14)	1593 (19)	135 (10)
C(12B)	1293 (21)	234 (18)	2243 (22)	211 (16)
C(15A)	-654 (12)	5231 (10)	-1191 (14)	94 (7)
C(15B)	-370 (16)	5826 (13)	-963 (18)	140 (10)
C(16A)	2414 (17)	1332 (14)	816 (20)	143 (10)
C(16B)	3068 (21)	1361 (18)	472 (26)	216 (17)
C(17A)	2071 (9)	2836 (9)	-732 (11)	67 (5)
C(17B)	2660 (12)	3200 (10)	-245 (14)	103 (7)
C(18A)	1450 (15)	4649 (12)	-1176 (16)	115 (8)
C(18B)	1726 (17)	4769 (14)	-1901 (20)	154 (11)
C(19A)	1527 (14)	2038 (14)	2511 (15)	118 (9)
C(19B)	1051 (17)	2014 (15)	3211 (19)	155 (11)
C(20A)	977 (9)	3582 (8)	1769 (11)	64 (5)
C(20B)	1698 (11)	3852 (10)	2129 (14)	97 (7)
C(21A)	677 (13)	5082 (13)	732 (17)	125 (9)
C(21B)	130 (16)	5419 (13)	1205 (18)	148 (11)

[a] The equivalent isotropic thermal parameters for the metal and oxygen atoms were estimated as one-third of the trace of U.

Discussion and Results

The molecular packing can be considered as body-centered cubic. As there are no plausible intermolecular hydrogen bonds, the structure is held together mostly by conventional van der Waals forces, giving a relatively low packing efficiency. The shortest intermolecular contact distance between the non-hydrogen atoms is 3.78 Å.

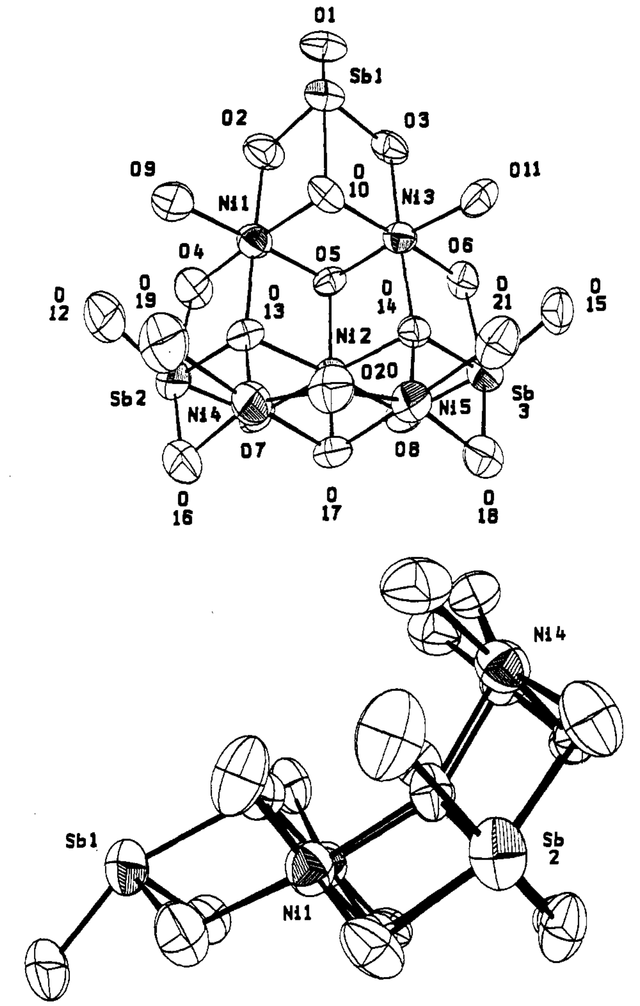

Figure 1. (a, Top) ORTEP drawing of the molecular structure of $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$ viewed perpendicular to the plane of the Sb atoms, showing the atom numbering scheme. The ethyl groups are omitted for clarity. (b, Bottom) similar to Figure 2a, but viewed parallel to the plane of the Sb atoms.

The wedge-shaped molecular conformation obtained, together with the atomic numbering scheme used for the metal and oxygen atoms, is shown in Figure 1a. By disregarding the apical Sb, a molecular fragment with a structure similar to that observed in $Ti_7O_4(OEt)_{20}$[9-11] is obtained. The methylene and methyl carbon atoms of each ethoxy group are labeled A and B respectively, preceded by the numbering of the corresponding oxygen atom. As the molecule contains two oxy oxygens (μ_4-O), the molecular formula must be $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$, assuming divalent nickel, trivalent antimony, and divalent oxygen atoms. By taking into account the metal coordination around the oxygen atoms, the molecular formula becomes $Ni_5Sb_3(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_3(\mu\text{-}OEt)_9(OEt)_3(HOEt)_4$. It has been suggested that the occurrence of oxy oxygens in related compounds might originate from partial hydrolysis with water or decomposition of organic molecules.[1]

From Figure 1b, it is clear that the three antimony atoms and three of the five nickel atoms (Ni(1), Ni(2), Ni(3)) are roughly coplanar. The largest deviation out of the least-squares plane through these six metal atoms is -0.06 Å. The Sb(2) and Sb(3) antimony atoms, Ni(2), and the remaining two nickel atoms Ni(4)

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(9) Watenpaugh, K.; Caughlan, C. N. *J. Chem. Soc., Chem. Commun.* **1967**, 76–77.

(10) Schmid, R.; Mosset, A.; Galy, J. *J. Chem. Soc., Dalton Trans.* **1991**, 1999–2005.

(11) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Park, C. W.; Rosenberg, D. S. *J. Am. Chem. Soc.* **1991**, *113*, 8190–8192.

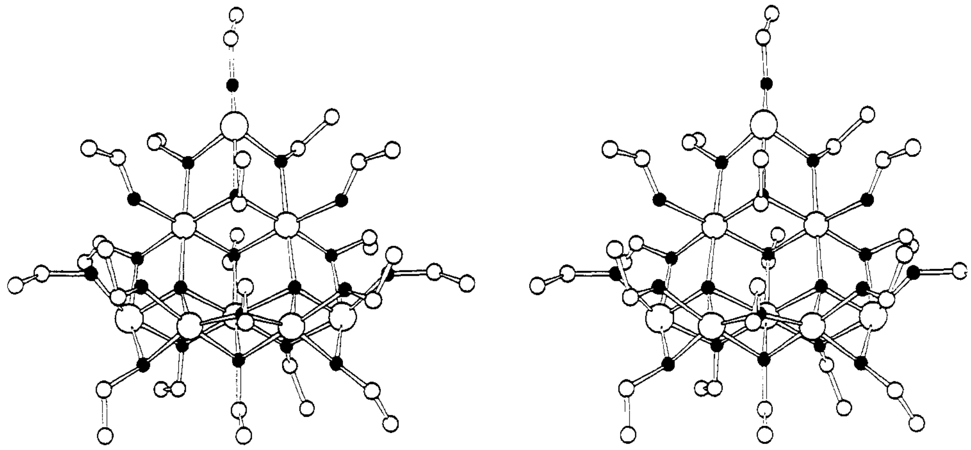

Figure 2. Stereoview of $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$ molecule including ethoxy carbon atoms. Hydrogens are omitted for clarity.

Table III. Metal–Oxygen Bond Distances (Å)[a]

Sb(1)–O(1)	2.01	Ni(2)–O(5)	2.09
Sb(1)–O(2)	1.98	Ni(2)–O(7)	2.06
Sb(1)–O(3)	1.98	Ni(2)–O(8)	2.05
Sb(1)–O(10)	2.32	Ni(2)–O(13)	2.14
		Ni(2)–O(14)	2.15
Sb(2)–O(4)	2.14	Ni(2)–O(17)	2.10
Sb(2)–O(7)	2.12		
Sb(2)–O(12)	2.32	Ni(3)–O(3)	2.11
Sb(2)–O(13)	1.99	Ni(3)–O(5)	2.06
Sb(2)–O(16)	2.17	Ni(3)–O(6)	2.02
		Ni(3)–O(10)	2.09
Sb(3)–O(6)	2.16	Ni(3)–O(11)	2.13
Sb(3)–O(8)	2.11	Ni(3)–O(14)	2.06
Sb(3)–O(14)	1.98		
Sb(3)–O(15)	2.33	Ni(4)–O(13)	2.02
Sb(3)–O(18)	2.17	Ni(4)–O(16)	1.96
		Ni(4)–O(17)	2.02
Ni(1)–O(2)	2.12	Ni(4)–O(19)	2.08
Ni(1)–O(4)	2.02	Ni(4)–O(20)	1.92
Ni(1)–O(5)	2.07		
Ni(1)–O(9)	2.14	Ni(5)–O(14)	2.03
Ni(1)–O(10)	2.08	Ni(5)–O(17)	2.01
Ni(1)–O(13)	2.06	Ni(5)–O(18)	1.98
		Ni(5)–O(20)	1.94
		Ni(5)–O(21)	2.07

[a] The esd's are about 0.01 Å.

and Ni(5) are also almost coplanar (maximum deviation −0.06 Å). A least-squares plane through these atoms forms an angle of 86° with the previous plane. The three antimony atoms are located in the corners of an almost equivalent triangle (Sb···Sb distances from 6.4 to 6.5 Å), with the three nickel atoms bisecting the edges of the triangle (cf. Figure 1a). Disregarding the ethyl groups, the molecule has an approximate noncrystallographic *m* symmetry (Figure 1a). The mirror plane is perpendicular to the least-squares plane through Sb(1), Sb(2), Sb(3), Ni(1), Ni(2), and Ni(3) and passes through the Sb(1) and Ni(2) atoms.

There are no short intermolecular contacts indicating hydrogen bonds in the structure. Therefore, the four ethanols of the molecule ought to be involved in intramolecular hydrogen bonds. The shortest intramolecular O···O contacts (2.52–2.54 Å) occur between the oxygen atoms O(15)···O(21), O(11)···O(15), O(12)···O(19), and O(12)···O(9) belonging to the terminal ethoxy groups of adjacent metal ions (see Figures 1 and 2). A probable hydrogen bond scheme would be that two hydrogen bonds connect O(9) with O(12) and O(12) with O(19) and two *m*-related ones connect O(11) with O(15) and O(15) with O(21). The quality of the diffraction data did not allow an unambiguous determination of the positions of the hydrogens involved in the hydrogen bonds. Consequently, it is not possible to determine which oxygen atoms act as acceptor and donor atoms to the hydrogen bonds.

The antimony atom Sb(1) is four-coordinated by oxygen atoms, while the Sb(2) and Sb(3) atoms both are five-coordinated. All antimony atoms appear to be trivalent (cf. discussion of bond valence sums below), and their stereoactive lone pairs give coordination geometries (Figure 1a) as expected around trivalent antimony ions. Thus, the Sb(1) atom is located in a distorted trigonal bipyramid where the lone pair occupies one of the equatorial geometrical positions. The Sb(2) (and Sb(3)) antimony atom is located in an octahedron with one of the coordination positions occupied by its lone pair. The shortest Sb(2)–O bond (and Sb(3)–O) occurs opposite to the Sb lone pair direction and is formed to the only μ_4-oxygen type in the structure. The Sb(2) (and Sb(3)) atom is displaced (0.5 Å) toward the lone pair region.

The nickel atoms Ni(4) and Ni(5) are five-coordinated by oxygen atoms in the form of distorted square pyramids where the apex atoms are the μ_4-oxygen atoms. The remaining three nickel atoms (Ni(1), Ni(2), Ni(3)) are all approximately octahedrally six-coordinated, with O–Ni–O angles between the adjacent oxygens ranging from 75.8 to 105.6°. The ethoxy μ_3-oxygen atoms are approximately tetrahedrally surrounded by three metal atoms and the adjacent carbon atom. The μ-oxygens O(2), O(3), and O(20) have rather coplanar surrounding atoms (<0.1 Å) possibly indicating a significant π bond contribution. The metal–oxygen bond distances are listed in Table III. The average Sb–O bond distances are 2.074, 2.149, and 2.151 Å for Sb(1), Sb(2), and Sb(3), respectively. These values agree well with the standard values for trivalent antimony ions[12] and give estimated bond valence sums,[13] bvs values, close to 3 (viz. 3.25, 3.24, and 3.24). The average Ni–O bond distances are 2.082, 2.099, 2.079, 2.002, and 2.006 Å for Ni(1–5) respectively, giving bvs values close to 2 (viz. 1.90, 1.81, 1.91, 1.97, and 1.94). Remarkably short Ni–O (<1.95 Å) distances to the two nickel atoms Ni(4) and Ni(5) from the oxygen atom O(20) are observed, possibly again indicating a higher π contribution in these bonds. The distribution of the nickel–oxygen bond distances are related to the coordination number of the oxygen atom. Thus, for μ_4-, μ_3-, and μ-oxygen atoms the nickel–oxygen distances (rms values within parentheses) are 2.08 (5), 2.06 (3), and 2.02 (7) Å, respectively.

As expected, the thermal vibrations increase along the ethoxy groups toward the methyl end. In the present case, the relatively weak van der Waals forces will allow the ethoxy groups to have relatively large thermal vibrations. These vibrations can also be expected to be anisotropic. However, the number of significant reflections observed is too small to permit a refinement where all the non-hydrogen atoms vibrate anisotropically (yielding 804 parameters for 3049 observations). Thus, the molecular geometry of the ethoxy groups is slightly unreliable. The O–C and C–C bond distances vary from 1.29 to 1.50 Å and 1.15 to 1.54 Å respectively, while the bond angles for O–C–C vary between 109.1 and 131.9°. However, the molecular geometry of the complex

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(12) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(13) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244–247.

as defined by the metal and oxygen atom positions is expected to be well established.

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Supplementary Material Available: A table of crystallographic data, listings of anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for the hydrogen atoms, calculated bond distances, angles, and planes, and figures showing the molecular packing in the crystal structure (8 pages); a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Contribution from the Departamento de Química Inorgánica and Laboratorio de Difracción de Rayos X,
Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, Spain, Instituto de Ciencias de Materiales,
Sede D, CSIC, Serrano 113, 28006-Madrid, Spain, and Departamento de Química Inorgánica, Facultat de Química,
Universidad de Valencia, Doctor Moliner 50, 46100-Burjasot, Valencia, Spain

Studies on the Reactivity of S,N-Derivatives of Nickel with N-Donor Bases. Crystal Structure and Magnetic Properties of the Cubane Cluster Tetrakis(μ-hydroxo)tetrakis(μ-1,3-thiazolidine-2-thionato)tetrakis(pyridine)-tetranickel(II)–Dipyridine

Loreto Ballester,[*,†] Eugenio Coronado,[‡] Angel Gutiérrez,[†] Angeles Monge,[§] Maria Felisa Perpiñán,[†] Elena Pinilla,[†] and Teresa Rico[†]

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The reaction of polymeric $[Ni(tzdt)_2]$ (tzdt = 1,3-thiazolidine-2-thionate) with pyridine affords two different compounds depending on the conditions employed: $[Ni(tzdt)_2(py)_2]$ in dry pyridine and $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$ with an excess of water. The former, mononuclear and paramagnetic, shows the nickel atom in an octahedral environment, while the latter has a cubanelike structure crystallizing in the tetragonal system: space group $P\bar{4}2_1c$, $Z = 8$, $a = 11.969$ (5) Å, $c = 18.357$ (9) Å, and $V = 2629$ (2) Å^3. The magnetic susceptibility of this cubane has been measured in the range 295–4 K showing that the compound has a diamagnetic ground state. The magnetic exchange among the four nickel atoms has been modeled with the use of three parameters, four ferromagnetic interactions ($J_1 = 17.5$ cm^{-1}) and two antiferromagnetic ($J_2 = J_3 = -22$ cm^{-1}). These interactions are propagated by the hydroxo bridges and are dependent on the Ni–O–Ni angles. The antiferromagnetic behavior is explained in terms of the distortions induced in the cubane core by the tzdt bridging ligands leading to two different types of Ni–O–Ni, those of ca. 95–96° and those of 103°. It is proposed that the latter are associated with the antiferromagnetic couplings.

Introduction

In previous papers we have described the coordinative ability of anionic sulfur-donor ligands in nickel(II) complexes and their reactivity toward N- and P-donor bases,[1] the nature of the obtained species being dependent on the sulfur ligand and the Lewis base.

1,3-Thiazolidine-2-thione (tzdtH), that exists mainly in the thione form in neutral solutions, is also of interest because of the possibility of coordination as a unidentate, bidentate, or bridging ligand.[2] The bridge form has been found in diamagnetic $[Ni(tzdt)_2]$ with a polymeric square-planar structure.[3] This ability can be used to obtain polynuclear nickel(II) complexes, with magnetic exchange interactions, in particular nickel(II) tetramers with cubanelike $[Ni_4O_4]$ cores.[4-6]

In our studies on the reactivity of $[Ni(tzdt)_2]$ toward N-donors we have obtained a mononuclear $[Ni(tzdt)_2(py)_2]$ compound and a tetrameric hydroxo complex $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$. To our knowledge this is the first tetranuclear hydroxo–nickel complex. The other tetranuclear complexes of nickel consist of a $[Ni_4(OCH_3)_4]^{4+}$ cubane framework. Most of these exhibit ferromagnetic intracluster exchange interactions, a result that has been attributed to the fact that the bridge angles Ni–O–Ni are close to 90° (in the range 93–99°).[4,5] The only exception to this behavior has been found in the complex $[Ni_4(OMe)_4(O_2CMe)_2(tmb)_4]^{2+}$,[6] (tmb = 2,5-dimethyl-2,5-diisocyanohexane) which exhibits an overall antiferromagnetic behavior that has been attributed to the presence of bridge angles of ca. 101°. We present here the crystal structure and magnetic properties of $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$. The magnetic properties of this compound are also dominated by an antiferromagnetic exchange interaction as a consequence of the presence of unusual bridge angles of ca. 103° in the cubane cluster.

Experimental Section

Materials and Methods. 1,3-Thiazolidine-2-thione was purchased from Ega Chemie and recrystallized from hot water before use. Pyridine was supplied by Merck and distilled over sodium. $[Ni(tzdt)_2]$ was prepared according to a previously reported procedure.[3]

Elemental analyses were carried out by the Servicio de Microanálisis of the Universidad Complutense de Madrid. IR spectra were taken in KBr disks using a Perkin-Elmer 1300 or a Philips PU9712 spectrophotometer. Electronic spectra were recorded in solids using a Uvikon 620 spectrophotometer equipped with diffuse reflectance accessories. Magnetic measurements were carried out with a Faraday-type susceptometer equipped with a helium continuous-flow cryostat.

Preparation of Compounds. Bis(1,3-thiazolidine-2-thionato)bis(pyridine)nickel(II), $[Ni(tzdt)_2(py)_2]$. $[Ni(tzdt)_2]$ (0.5 mmol) was dissolved in 5 mL of pyridine and the solution was stirred for 1 h, forming the adduct as a green microcrystalline solid that precipitated completely by addition of diethyl ether to the pyridine solution. The solid was collected, washed with a pyridine/diethyl ether mixture, and dried in vacuo. A quantitative yield was obtained.

Anal. Calc for $C_{16}H_{18}N_4NiS_4$: C, 42.4; H, 3.9; N, 12.4. Found: C, 42.4; H, 3.9; N, 12.0. IR (cm^{-1}): 3040 (w), 2920 (w), 2850 (m), 1600 (s), 1506 (s), 1480 (m), 1440 (s), 1295 (s), 1215 (s), 1070 (s), 1024 (s), 978 (s), 930 (m), 755 (s), 690 (s), 660 (m), 625 (m), 435 (m). UV–vis (nm): 760, 610, 360, 300, 212.

[†] Departamento de Química Inorgánica, Universidad Complutense Madrid.

[‡] Departament de Química Inorgánica, Universidad de Valencia.

[§] Laboratorio de Difracción, CSIC Madrid.

(1) (a) Ballester, L.; Gutiérrez, A.; Pérez, S.; Perpiñán, M. F. *Inorg. Chem.* **1991**, *30*, 2954. (b) Ballester, L.; Gutiérrez, A.; Perpiñán, M. F.; Gutiérrez-Puebla, E.; Ruiz-Valero, C. *Polyhedron* **1990**, *9*, 1341. (c) Perpiñán, M. F.; Ballester, L.; Gonzalez-Casso, M. E.; Santos, A. *J. Chem. Soc., Dalton Trans.* **1987**, 281.

(2) Raper, E. S. *Coord. Chem. Rev.* **1985**, *61*, 115.

(3) Preti, C.; Tosi, G. *Can. J. Chem.* **1976**, *54*, 1558.

(4) Bertrand, J. A.; Ginsberg, A. P.; Kapaln, R. I.; Kirkwood, C. E.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem.* **1971**, *10*, 240.

(5) Andrew, J. E.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1456.

(6) Gladfelter, W. L.; Lynch, M. W.; Schaefer, W. P.; Hendrickson, D. N.; Gray, H. B. *Inorg. Chem.* **1981**, *20*, 2390.

0020-1669/92/1331-2053$03.00/0