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Synthetic and Structural Studies of a New Nickel-Antimony Alkoxide: $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$

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A Ni-Sb alkoxide of the formula $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$ has been prepared by reacting anhydrous $NiBr_2$ with 2KOEt and $Sb(OEt)_3$ in a toluene/ethanol solution under a dry, oxygen-free atmosphere. $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$ crystallizes with the centrosymmetric tetragonal space group symmetry $P4_2/n$, with $a = 13.003(1)$ Å, $c = 19.332(3)$ Å, $V = 3269(1)$ Å^3, $Z = 2$, $D_x = 1.833(1)$ g/cm^3, and $M = 1808.6$. The crystal structure was refined to $R = 0.036$ ($R_w = 0.039$) for the 3005 most significant single-crystal X-ray diffraction intensities collected with Mo Kα radiation (λ(Mo Kα) = 0.7107 Å, μ(Mo Kα) = 34.0 cm^{-1}) at 170(1) K. The packing of the molecules can be considered as body-centered cubic. The trivalent Sb atoms are 5-coordinated by oxygen atoms; the stereoactive lone pair completes an octahedral coordination geometry. The nickel atoms are approximately octahedrally coordinated by the oxygen atoms. Strong intramolecular hydrogen bonds, involving the hydroxyl groups of the ethanol molecules, apparently affect the molecular geometry. Extended Hückel molecular orbital calculations further support the assignment of the intramolecular hydrogen bond. An analysis of the thermal vibrational parameters indicates that all the metal and oxygen atoms in the molecule can be considered as constituting an essentially rigid body, while the thermal motions of the ethyl groups are more uncorrelated.

Introduction

Since the 1960s there has been a growing interest in bimetallic alkoxide chemistry, first from a basic research perspective and later from more applied perspectives such as sol-gel processing of ceramic materials and preparation of various catalysts.[1]

Even if a large number of bimetallic alkoxides have been synthesized, the amount of reliable molecular structural information is sparse.[2] Such information is of course important for any future attempts to correlate the molecular structure to various properties such as stoichiometry and chemical reactivity. Thus far, in the field of bimetallic tervalent antimony alkoxides a few bimetallic alkoxides have been synthesized,[3-6] but the crystal structures are known for only two of them, $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$[7] and $Mg_2Sb_4(OEt)_{16}$.[8]

Systematic studies of a bimetallic alkoxide system, like the Ni^{2+}-Sb^{3+} ethoxides, is complicated by the formation of several complexes containing different Ni:Sb ratios and oxo oxygens. Here we report on a structural study of a Ni-Sb ethoxide formed with a Ni:Sb ratio of 3:2. The compound is formed by reacting $NiBr_2$ with 2KOEt and $Sb(OEt)_3$[3,4] in a toluene/ethanol solution. In a previous article[7] concerning the structure of $Ni_5Sb_3O_2(OEt)_{15}(EtOH)_4$, it was reported that both squarish yellow crystals of $Ni_5Sb_3O_2(OEt)_{15}(EtOH)_4$ and green needles of an unknown composition were formed. Although somewhat different preparation conditions have been applied, the green Ni-Sb ethoxide described in the present paper is most probably identical to the previously described[7] green specimen, as they have similar IR spectra and chemical behaviors.

The present investigation is a part of a research program concerning the synthesis, characterization, and properties of M^{2+}-Sb^{3+} ethoxides. Studies of the magnetic properties of several transition metal-Sb^{3+} ethoxides are in progress.

Experimental Section

Preparation. All preparations and the mounting 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 $Mg(OEt)_2$ or CaH_2, respectively. $Sb(OEt)_3$ was prepared by reacting $SbCl_3$ with NH_3 gas in ethanol and hexane.[9] The crude $Sb(OEt)_3$ was then distilled in vacuum. KOEt was prepared by dissolving K in toluene/ethanol.[3,4]

A 5.04-g sample of $Sb(OEt)_3$ was added to a toluene/ethanol (4:1) mixture (80 mL) containing 3.27 g of KOEt. After approximately 24 h 4.24 g of anhydrous $NiBr_2$ was added, and reaction was allowed to proceed for 1 week at room temperature, yielding a brownish yellow solution and precipitated KBr. On slow evaporation of the solution, small amounts of yellow crystals, identified as the previously[7] studied $Ni_5Sb_3O_2(OEt)_{15}(EtOH)_4$, were first formed. The remaining yellowish solution was then further evaporated, yielding a green microcrystalline specimen. On recrystallization from a toluene/ethanol (4:1) solution by very slow evaporation and subsequent additions of ethanol, crystals suitable for X-ray diffraction studies were obtained. IR spectra before and after recrystallization were identical. The green crystals turned yellow with subsequent devitrification within minutes when brought out of the solvent. They also turned yellow within a few minutes in a mixture with dry KBr and almost immediately on dissolving in paraffin oil and in toluene/ethanol (4:1). The greenish color is maintained by rapidly pressing a tablet of the KBr mixture. Attempts to obtain a melting point of the substance in a sealed glass capillary resulted in devitrification and color change to yellow in the temperature range 40-55 °C and blackening in the range 200-205 °C without melting.

The green crystal chosen for the X-ray study was cut into a suitable size and transferred as quickly as possible to a glass capillary containing minor amounts of ethanol. The capillaries were then sealed inside the glovebox. Our experiences have shown that the ethanol content prevents devitrification and minimizes the crystal reorientations during the low-temperature X-ray data collection, by "gluing" the crystals to the capillary walls.

Structure Determination. Preliminary investigations of a selected crystal by means of a STOE single-crystal X-ray diffractometer (Mo Kα radiation) indicated primitive tetragonal space group symmetry. The

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Table I. Crystallographic Data for $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$

formula	$Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$
fw	1808.4
space group	$P4_2/n$ (No. 86)
unit cell dimens	$a = 13.003(1)$ Å $b = 13.003(1)$ Å $c = 19.332(3)$ Å
unit cell vol, V	3269(1) Å^3
formula units per unit cell, Z	2
calcd density, D_x	1.833(1) g cm^{-3}
wavelength, λ (Mo Kα)	0.710 73 Å
temp, T	170(1) °C
linear abs coeff, μ	34.0 cm^{-1}
2θ range	60°
ranges of h, k, and l	−1 to 17, 0 to 17, and 0 to 23
transm factor range	0.49–0.64
final R^a for obsd refls	0.034
final $R_w{}^b$ for obsd refls	0.037

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

Table II. Fractional Atom Coordinates (×10^4) and Isotropic Thermal Parameters from the Refined Anisotropic Parameters (×10 Å^2) for the Non-Hydrogen Atoms (with Esd's)[a]

atom	x	y	z	U_{eq}
Sb(1)	4053(1)	4382(1)	1433(1)	18(1)
Ni(1)	2500	2500	3658(1)	16(1)
Ni(2)	2721(1)	4390(1)	2733(1)	16(1)
O(1)	3404(2)	1660(2)	2975(2)	17(1)
O(2)	3472(2)	3799(2)	3580(2)	19(1)
O(3)	3425(3)	1701(3)	4315(2)	22(1)
O(4)	5177(3)	941(3)	2572(2)	21(1)
O(5)	3336(3)	−211(2)	3386(2)	21(1)
O(6)	2887(3)	−4(2)	1815(2)	21(1)
C(2A)	3669(4)	4387(4)	4193(3)	25(1)
C(2B)	4197(5)	5397(5)	4051(3)	30(2)
C(3A)	3796(4)	1964(5)	4972(3)	34(2)
C(3B)	3607(7)	1179(7)	5511(4)	53(3)
C(4A)	6258(4)	833(5)	2645(3)	29(2)
C(4B)	6594(5)	−259(5)	2549(4)	42(2)
C(5A)	3523(4)	−1258(4)	3573(3)	30(2)
C(5B)	3477(5)	−1424(5)	4345(3)	36(2)
C(6A)	3444(5)	−954(4)	1784(3)	28(2)
C(6B)	3483(6)	−1372(5)	1051(3)	39(2)

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

unit cell parameters were determined and refined from diffractometer-determined θ values as $a = 13.003(1)$ and $c = 19.332(3)$ Å.

Single-crystal X-ray diffraction data were collected and corrected for background, Lorentz, polarization, and absorption effects. The absorption correction was performed with the program STOEABS written by R.N. Intensity statistics indicated a centrosymmetric space group symmetry. The selected space group symmetry $P4_2/n$, deduced from the systematic extinctions in the diffraction data, 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.[10] The remaining atomic positions were found from subsequent calculations of difference electron density ($\Delta\rho$) maps. In the final least-squares refinement all the non-hydrogen atoms were allowed to vibrate anisotropically, while the methylene and methyl hydrogen atoms were restricted to isotropic vibrations. As expected, the thermal vibrations increased along the ethoxy groups.

Details on the experimental conditions and the final structural refinements are given in Table I. Least-squares refinements of the structural model yielded an R value of 0.036 ($R_w = 0.039$). The final atomic coordinates with thermal parameters, bond distances, and bond angles are listed in Tables II–IV, respectively. The methylene and methyl carbon atoms of the ethoxy groups hae 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 package,[11] using atomic scattering factors for neutral atoms from ref 12.

IR Investigation. Infrared spectra of freshly prepared specimens of $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$ in KBr and in paraffin solution were collected with a Mattson Polaris FT-IR instrument from 4000 to 400 cm^{-1}. At the higher wavenumbers (>1200 cm^{-1}), the vibrations of ethyl groups and hydrogen bonds could be observed, while those of the carbon–oxygen (C–O) and metal–oxygen (M–O) bonds were observed in the range 1200–400 cm^{-1}. The ethyl vibrations are quite similar to those reported by Lutz for $Mg(OEt)_2$.[13] A broad band with a maximum at 2516 cm^{-1} indicates the presence of strong hydrogen bonds, confirmed by the X-ray studies. The spectrum for a KBr tablet with its greenish color can be expected to represent the solid-state molecular structure, while the spectrum of the paraffin solution with its yellowish color represents a solution structure. The two spectra covering the C–O and M–O regions are shown in Figure 1. The spectra are similar in the M–O regions, indicating that the metal–oxygen core structures of the two molecular specimens are similar.

Table III. Intramolecular Distances (Å, with Esd's) between Non-Hydrogen Atoms

Sb(1)–O(1)	1.95(1)	Sb(1)–O(5)	2.06(1)
Sb(1)–O(3)	2.14(1)	Sb(1)–O(6)	2.75(1)
Sb(1)–O(4)	2.18(1)		
Ni(1)–O(1)	2.08(1)	Ni(1)–O(2)	2.11(1)
Ni(1)–O(1)	2.08(1)	Ni(1)–O(3)	2.04(1)
Ni(1)–O(2)	2.11(1)	Ni(1)–O(3)	2.04(1)
Ni(2)–O(1)	2.06(1)	Ni(2)–O(4)	2.10(1)
Ni(2)–O(1)	2.04(1)	Ni(2)–O(5)	2.15(1)
Ni(2)–O(2)	2.06(1)	Ni(2)–O(6)	2.10(1)
O(2)–C(2A)	1.43(1)	C(2A)–C(2B)	1.51(1)
O(3)–C(3A)	1.40(1)	C(3A)–C(3B)	1.49(1)
O(4)–C(4A)	1.42(1)	C(4A)–C(4B)	1.50(1)
O(5)–C(5A)	1.43(1)	C(5A)–C(5B)	1.51(1)
O(6)–C(6A)	1.43(1)	C(6A)–C(6B)	1.52(1)

Table IV. Selected Intramolecular Bond Angles (deg, with Esd's)

O(1)–Sb(1)–O(3)	78.5(1)	O(3)–Sb(1)–O(5)	93.8(1)
O(1)–Sb(1)–O(4)	98.0(1)	O(3)–Sb(1)–O(6)	86.1(1)
O(1)–Sb(1)–O(5)	79.5(1)	O(4)–Sb(1)–O(5)	99.3(1)
O(1)–Sb(1)–O(6)	66.3(1)	O(4)–Sb(1)–O(6)	68.1(1)
O(3)–Sb(1)–O(4)	150.5(1)	O(5)–Sb(1)–O(6)	145.1(1)
O(1)–Ni(1)–O(1)	101.1(1)	O(2)–Ni(1)–O(3)	95.7(1)
O(1)–Ni(1)–O(2)	82.7(1)	O(2)–Ni(1)–O(3)	89.5(1)
O(1)–Ni(1)–O(2)	92.1(1)	O(3)–Ni(1)–O(3)	102.7(1)
O(1)–Ni(1)–O(3)	78.1(1)		
O(1)–Ni(2)–O(1)	90.9(1)	O(1)–Ni(2)–O(6)	100.1(1)
O(1)–Ni(2)–O(2)	96.4(1)	O(2)–Ni(2)–O(4)	90.8(1)
O(1)–Ni(2)–O(2)	84.8(1)	O(2)–Ni(2)–O(5)	91.3(1)
O(1)–Ni(2)–O(4)	78.0(1)	O(4)–Ni(2)–O(5)	116.8(1)
O(1)–Ni(2)–O(5)	75.1(1)	O(4)–Ni(2)–O(6)	83.6(1)
O(1)–Ni(2)–O(6)	79.7(1)	O(5)–Ni(2)–O(6)	93.8(1)
Sb(1)–O(3)–C(3A)	121.6(3)	Sb(1)–O(5)–C(5A)	120.1(3)
Sb(1)–O(4)–C(4A)	112.5(3)	Sb(1)–O(6)–C(6A)	134.8(3)
Ni(1)–O(2)–C(2A)	118.3(3)	Ni(2)–O(2)–C(2A)	122.8(3)
Ni(1)–O(2)–C(2A)	118.3(3)	Ni(2)–O(4)–C(4A)	126.4(3)
Ni(1)–O(3)–C(3A)	130.0(3)	Ni(2)–O(5)–C(5A)	136.9(3)
Ni(1)–O(3)–C(3A)	130.0(3)	Ni(2)–O(6)–C(6A)	123.6(3)
O(2)–C(2A)–C(2B)	113.5(4)	O(5)–C(5A)–C(5B)	112.4(5)
O(3)–C(3A)–C(3B)	113.9(6)	O(6)–C(6A)–C(6B)	111.3(5)
O(4)–C(4A)–C(4B)	111.8(5)		

Results and Discussion

The roughly spherically shaped molecules (Figure 2) are packed in a body-centered arrangement. As there are no indications of intermolecular hydrogen bonds, the crystal structure is held together mostly by van der Waals forces. The shortest intermolecular contact distance between non-hydrogen atoms is 3.78 Å.

The obtained molecular geometry is shown in Figure 2 together with the atomic labels used for the metal and oxygen atoms. The bond distance distributions and calculated bond valence sums[14,15] (bvs values) indicate that the Ni atoms are divalent and the Sb

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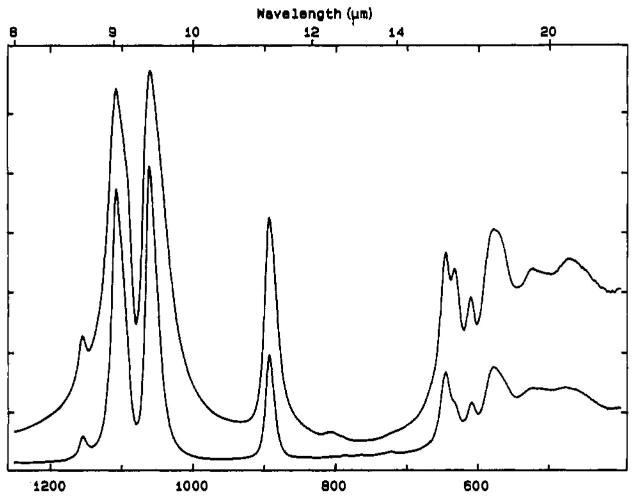

Figure 1. FT-IR spectra of $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$ in a KBr tablet (upper) and paraffin solution (lower).

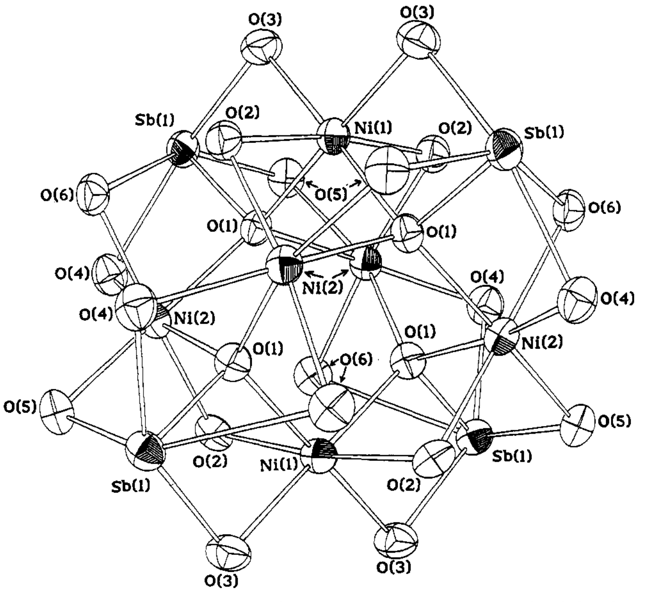

Figure 2. ORTEP drawing of the molecular structure of $Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4$ viewed perpendicular to the 4-fold roto-reflection axis through the two Ni(1) atoms. The thermal ellipsoid sizes correspond to the 70% positional probability surface.

atoms trivalent. As the structure determination shows that each molecule consists of six Ni atoms, four Sb atoms, and twenty ethoxy groups, four of the ethoxy groups have to be protonated to achieve electroneutrality. Thus, the molecular formula becomes $Ni_6Sb_4O_4(OEt)_{16}(EtOH)_4$. Taking the metal coordination around the oxygen atoms into account, the molecular formula is $Ni_6Sb_4(\mu_4\text{-}O)_4(\mu_2\text{-}OEt)_{16}(HOEt)_4$. The appearance of oxo oxygens is apparently a common occurrence in many metal alkoxides, and it has been suggested that it might originate[2] either from internal decomposition or possibly from the presence of minor traces of water or oxygen.

Due to the space group symmetry, the molecules have the point symmetry S_4, with the 4-fold roto-reflection axis along the two (Ni(1) atom positions ($^1/_4$, $^1/_4$, z) and with the mirror plane halfway between them (x, y, $^1/_4$). The metal atom positions in the molecule can be imagined approximately as a tetrahedral arrangement of the four Sb atoms, with six Ni atoms located roughly on the midpoint of the edges of the Sb tetrahedron. In this way, the Ni arrangement becomes approximately octahedral. The metal ions are bridged by bonds to the oxygen atoms, forming a rather globular molecular shape. The coordination polyhedra that share edges given metal···metal distances of 3.178(1), 3.052(1), and 3.052(1) Å for Sb(1)···Ni(1), Sb(1)···Ni(2), and Ni(1)···Ni(2), respectively.

The molecular structure of the present Ni–Sb ethoxide is related to that observed for the Pb–Nb ethoxide $Pb_6Nb_4O_4(OEt)_{24}$.[16] However, the arrangements of the oxygen atoms in the two ethoxides differ, as one of the ethoxy groups coordinating the Nb atom in the Pb–Nb ethoxide is "replaced" by a lone pair in the present Ni–Sb ethoxide. Furthermore, the metal–oxygen bonding to the two oxygen atoms O(2) and O(6) in the Ni–Sb ethoxide is different due to the presence of the intramolecular O(2)···O(6) hydrogen bond (see below).

Only one symmetry-independent Sb atom is present in the molecule. The Sb atoms have four short (1.95–2.18 Å) bond distances and one long (2.75 Å) bond distance to oxygen atoms. The coordination geometry is completed by the stereoactive lone pair obviously pointing out from the molecule. As observed in the study of the Ni–Sb ethoxide $Ni_5Sb_3O_2(OEt)_{15}(EtOH)_4$,[7] the shortest Sb–O bond is found opposite to the expected Sb lone pair direction. This Sb–μ_4-O(1) distance is close to that found in $Ni_5Sb_3O_2(OEt)_{15}(EtOH)_4$. There are two symmetry-independent nickel atoms in the molecule, both with approximately octahedral coordinations. The distributions of Ni–O distances and O–Ni–O angles (2.04(1)–2.15(1) Å, 78.0(1)–116.8(1)°) are very close to those of e.g. the octahedral Ni atoms in $Ni_5Sb_3O_2(OEt)_{15}(EtOH)_4$[7] (2.02(2)–2.15(1) Å, 75.8(4)–105.6(4)°). The μ_4-oxo oxygens, O(1), are tetrahedrally coordinated by one Sb and three Ni atoms.

Since there are no indications of intermolecular hydrogen bonds, the four hydrogen atoms of the ethanol hydroxyl groups in the molecule ought to be involved in intramolecular hydrogen bonds. To avoid strong electrostatic repulsion, between positively charged metal ions and the hydroxyl hydrogen, such a hydrogen bond is most likely to be formed between oxygen atoms coordinating different adjacent metal ions. In the molecule there are only three such suitable O···O contacts present, viz. O(2)···O(6), O(2)···O(4), and O(5)···O(6) (distances 2.44(1), 4.74(1), and 3.11(1) Å, respectively). A difference electron density ($\Delta\rho$) map along the O(2)–O(6) vector shows a reasonably high value at an expected hydrogen position (0.6 e/Å^3) of a hydrogen bond. The very short distance of 2.44 Å between the O(2) and O(6) atoms indicates a very strong linear hydrogen bond. Accordingly, the hydrogen position was assumed to be located halfway between these oxygen atoms[17] and was constrained to this position in the final structural refinement. The presence of this hydrogen bond obviously affects the molecular geometry by tying two oxygens from different coordination polyhedra very closely together. The ethoxy groups of the molecule show normal bond distances and angles. The averages of the O–C and C–C bond distances and of the O–C–C angles are 1.42(1) Å, 1.51(1) Å, and 113(1)°, respectively.

Semiempirical molecular orbital (MO) calculations of the extended Hückel type[18,19] were performed for the experimental molecular geometry of the entire molecule using the parameters compiled by Alvarez.[20] The extended Hückel method is a very approximate MO method. Some support[8] for the relevance of the derived atomic charges, when estimated as gross atomic electron populations, is the fact that the charges from extended Hückel calculations on e.g. the $Al_2(OH)_6$ molecule agree well

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with the charges obtained by more rigorous ab initio calculations. Hückel calculations for the observed molecular geometry of the present Ni–Sb ethoxide give atomic charges of +1.7, +1.3, and +0.9 for the Sb, Ni(1), and Ni(2) atoms, respectively. Except for the very long Sb–O(6) bond (2.75 Å), all the Sb–O overlap populations (0.2–0.4) are considerably higher than those of Ni–O (<0.2), in accordance with the expected less ionic character of the Sb–O bonds. When the hydrogen positions of the suggested ethanol hydroxyl group at O(6) are omitted (cf. above), the charges of the oxygen atoms O(1–6) of the anion become –1.2, –1.05, –0.9, –1.05, –0.9, and –1.2, respectively. A low charge on the O(1) atoms is to be expected, as the O(1) atoms are the only oxo oxygens in the molecule. The low estimated charge on the O(6) atom indicates that O(6) is the oxygen atom most likely to be protonated and to act as the hydrogen donor in a hydrogen bond. The short O(6)··O(2) distance (2.44 Å) and the relatively low charge on the O(2) atom make it the most likely hydrogen-bond acceptor. Accordingly, the Hückel calculations also (cf. above) indicate the intramolecular hydrogen bond to be O(6)–H··O(2).

The parameters describing the anisotropic thermal vibrations of the atoms were analyzed by the techniques described by Hirshfeld[21] and Rosenfield et al.,[22] for the presence of rigid groups of atoms within the molecule. The results indicate that all the oxygen and metal atoms of the molecule (cf. Figure 2) are vibrating as a rigid group. Thus, the average difference between the mean-square thermal displacement amplitudes along interatomic directions is only 0.0015 Å^2. With the program THMA11[23] the 6 independent parameters of the matrices describing the translation, libration, and screw motions of the metal and oxygen atoms were estimated. From these 6 parameters, the 54 observed thermal parameters could be reproduced within 3 esd's for all parameters except for the U_{33} parameter of the Ni(1) atom (5 esd's). The agreement (weighted R value of 0.040) between reproduced and observed thermal parameters supports the picture of the metal and oxygen atoms as an essentially rigid group. The corrections of the bond distances for rigid-body-motion effects are negligible (<0.0013 Å).

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Supplementary Material Available: Tables of crystallographic data, positional and anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for the hydrogen atoms, and calculated bond distances and angles and figures showing the molecular packing in the crystal structure and a stereoview of the molecule (10 pages). Ordering information is given on any current masthead page.

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