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Structural Characterization of

N,N'-Ethylenebis(1,1,1-trifluoroacetylacetonate iminato)nickel(II)

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The crystal and molecular structure of *N,N'*-ethylenebis(1,1,1-trifluoroacetylacetonate iminato)nickel(II), NiC₁₂H₁₂N₂O₂F₆, has been determined from three-dimensional counter x-ray data. The material crystallizes in the monoclinic space group *P*2₁/*c* with four formula units in a cell of dimensions *a* = 11.044 (8) Å, *b* = 17.116 (11) Å, *c* = 7.769 (5) Å, and β = 98.04 (4)°. Least-squares refinement of the structure has led to a final *R* factor (on *F*) of 0.047 using 1396 independent intensities. The structure consists of stacks of nearly parallel macrocycles, the Ni-Ni separation in the chain being 4.024 (3) Å. The coordination around each nickel(II) center is square planar, the average Ni-O and Ni-N bond lengths being 1.844 (4) and 1.860 (5) Å, respectively. The macrocyclic ligands are distinctly nonplanar, the principal distortion from planarity being a folding along an O-Ni-N vector. The ligand, which is the 2:1 condensation product of 1,1,1-trifluoro-2,4-pentanedione (tfacac) with ethylenediamine, has the CF₃ groups attached to the carbon atoms which are most distant from the imine linkage; i.e., the condensation took place at the 4 position of the tfacac ligand. The reported EPR spectrum of the analogous copper(II) complex doped in this host lattice is readily explained in the light of the observed structure.

Introduction

Transition metal complexes of Schiff base ligands are always of interest since they exhibit a marked tendency to oligomerize, thus leading to novel structural types, and also display a wide variety of magnetic properties. Many of the reported structural investigations of these complexes are discussed in some detail in a recent review.¹ Although the tetradentate Schiff base complexes of several metals and particularly of copper(II) have been well studied, there is a paucity of data concerning the nickel(II) analogues, and to our knowledge only one structural analysis of such a complex has been reported.²

N,N'-Ethylenebis(1,1,1-trifluoroacetylacetonate iminato)nickel(II), Ni[en(tfacac)₂], is a significant example of such complexes. The Schiff base ligand is expected to be similar to en(acac)₂, but its exact structure is uncertain since there are three different possible stereochemistries for the 2:1 condensation product of 1,1,1-trifluoro-2,4-pentanedione (tfacac) with en; these arise because the two oxygen atoms of each tfacac moiety are distinguishable, and each condensation might occur at either the 2 or the 4 position. On the basis of the NMR spectra of the pure ligand³ it has been suggested that the ligand is symmetric and that condensation probably occurred at the 2 position in each case.

The structure of this chelated complex is also of magnetic interest since it was observed by Lancione and Allen⁴ that Cu[en(tfacac)₂] doped in the nickel lattice yields only one magnetic site in contrast to the unfluorinated analogue,⁵ Cu[en(acac)₂] doped in Ni[en(acac)₂], which exhibited two. From this it is clear that in the former case the molecules either are constrained by space group symmetry or are fortuitously arranged such that all coordination planes are parallel. Thus,

since this complex promised to be revealing from several viewpoints, we have undertaken a complete three-dimensional structural analysis of Ni[en(tfacac)₂].

Experimental Section

Single crystals of Ni[en(tfacac)₂] suitable for x-ray analysis were generously provided by Drs. H. C. Allen and R. L. Lancione. After examination by precession and Weissenberg photography the crystals were assigned to the monoclinic system. Systematic absences were observed for *0k0* with *k* odd and *h0l* with *l* odd which uniquely determines the space group as *P*2₁/*c* (*C*_{2h}⁵). The cell constants obtained by least-squares methods⁶ are *a* = 11.044 (8) Å, *b* = 17.116 (11) Å, *c* = 7.769 (5) Å, and β = 98.04 (4)°; these observations were made at 20 °C with the wavelength assumed as λ(Cu Kα₁) = 1.5405 Å. The density of 1.79 g/cm³ calculated for four molecules in a unit cell is in good agreement with the value of 1.78 (2) g/cm³ observed by flotation in aqueous ZnBr₂. Hence, with four formula units per cell, no crystallographic symmetry need be imposed on the molecules.

Intensity data were collected from a parallelepiped-shaped crystal of dimensions 0.077 × 0.009 × 0.010 cm. The crystal was mounted along the long axis, which is parallel to the crystallographic *c* axis. The crystal mosaicity was examined in the usual way⁷ and found to be acceptable. The data were collected in a manner described elsewhere,⁸ using an automatic Picker four-circle diffractometer employing nickel-prefiltered copper radiation. The takeoff angle was 1.5°, the scan rate was 1.0°/min, and the scan range was from 0.6° below the calculated Kα₁ position to 0.6° above the calculated Kα₂ peak position; backgrounds were counted for 10 s on each end of the scan. A unique data set of 2297 reflections having 2θ(Cu) ≤ 128° was gathered; of these reflections, 1396 had intensities greater than 3 times their estimated standard deviations.

The data were processed in the usual manner.^{7,8} An absorption correction was applied; the linear absorption coefficient for this compound and Cu Kα radiation is 26.5 cm⁻¹. The transmission coefficients for the data crystal ranged between 0.70 and 0.90.⁹

Table I. Positional Parameters ($\times 10^4$) for Ni[en(tfacac)₂]

Atom	x	y	z
Ni ^a	-18 095 (7)	28 073 (5)	23 340 (11)
F(1)	-3 234 (4)	5 193 (2)	-852 (6)
F(2)	-3 497 (5)	5 129 (2)	-3 577 (7)
F(3)	-4 992 (3)	4 986 (2)	-2 189 (7)
F(4)	1 026 (4)	4 253 (2)	-4 325 (6)
F(5)	2 340 (3)	3 353 (3)	-4 365 (6)
F(6)	2 070 (4)	3 867 (3)	-1 992 (5)
O(1)	-423 (3)	3 340 (2)	-2 703 (5)
O(2)	-2 437 (3)	3 800 (2)	-2 157 (5)
N(1)	-3 248 (4)	2 302 (2)	-1 970 (6)
N(2)	-1 161 (4)	1 823 (2)	-2 620 (6)
C(1)	1 493 (6)	3 627 (4)	-3 488 (9)
C(2)	505 (5)	3 020 (3)	-3 239 (7)
C(3)	689 (5)	2 267 (3)	-3 539 (7)
C(4)	-142 (5)	1 662 (3)	-3 212 (7)
C(5)	202 (7)	828 (4)	-3 637 (9)
C(6)	-5 424 (6)	2 117 (4)	-1 676 (10)
C(7)	-4 308 (5)	2 615 (3)	-1 876 (7)
C(8)	-4 483 (5)	3 443 (4)	-1 937 (8)
C(9)	-3 560 (5)	3 950 (3)	-2 093 (7)
C(10)	-3 838 (6)	4 816 (4)	-2 175 (11)
C(11)	-1 943 (7)	1 201 (3)	-2 204 (10)
C(12)	-3 120 (7)	1 450 (4)	-1 926 (10)
H(1) ^b	1 461	2 127	-3 967
H(2)	-5 297	3 658	-1 857
H(3)	-2 057	814	-3 110
H(4)	-1 562	928	-1 166
H(5)	-3 281	1 289	-749
H(6)	-3 751	1 230	-2 713

^a Positional parameters for nickel atom $\times 10^5$. ^b Calculated positions for hydrogen atoms.

Solution and Refinement of the Structure. The position of the nickel atom was obtained from a three-dimensional Patterson map, and two cycles of least-squares refinement gave values of the usual residuals $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 0.55 and 0.61, respectively.

In all least-squares refinements in this analysis the function minimized was $\sum w(|F_o| - |F_c|)^2$, with the weight being assigned as $4F_o^2 / \sigma(F_o^2)$. In all calculations of F_c , the atomic scattering factors for Ni and F were from Cromer and Waber,¹⁰ those for O, N, and C were from Ibers,¹¹ and those for H were from Stewart, Davidson, and Simpson.¹² The effects of the anomalous dispersion of the Ni were included in the calculation of F_c ,¹³ the values $\Delta f'$ and $\Delta f''$ being taken from Cromer.¹⁴

The remaining nonhydrogen atoms were located in subsequent difference Fourier maps, and two cycles of isotropic least-squares refinement gave values of R_1 and R_2 of 0.16 and 0.20, respectively. Two additional cycles of least-squares refinement with anisotropic thermal parameters for all 23 atoms gave $R_1 = 0.07$ and $R_2 = 0.11$. From the following difference map it proved possible to locate the two ring hydrogen atoms and the four hydrogen atoms on the ethylene bridge, all of which were very close to their respective calculated positions. Although some residual density was apparent around each of the two methyl carbon atoms, it was not possible to assign reasonable hydrogen positions from this density. No attempt was made to refine the ring and ethylene bridge hydrogen atom positions; these were left in the calculated positions as a fixed contribution for the remainder of the refinement. Also several of the low-angle data were suffering from secondary extinction, so an extinction correction was applied.¹⁵ In the final cycle of least-squares refinement no parameter exhibited a shift of more than 0.06 times its estimated standard deviation, and this was taken as evidence that the refinement had converged. The final cycle involved full-matrix refinement of 209 variables using 1396 independent intensities; the final values of the residuals were $R_1 = 0.047$ and $R_2 = 0.061$. The positional and thermal parameters for all atoms are given in Tables I and II; the calculated positions of the ring and ethylene-bridge hydrogen atoms are also given in Table I. A table of observed and calculated structure amplitudes is available.¹⁶

Description of the Structure

The structure consists of a stacked arrangement of Ni[en(tfacac)₂] molecules leading to the formation of infinite chains. The trifluoro groups were found to be symmetrically

Table II. Thermal Parameters^a (U_{ij} , 10^{-3} Å²) for Ni[en(tfacac)₂]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni ^b	503 (6)	364 (4)	2174 (6)	5 (4)	17 (2)	40 (4)
F(1)	113 (3)	63 (2)	163 (4)	6 (2)	-3 (3)	-39 (3)
F(2)	165 (4)	66 (3)	149 (4)	29 (3)	54 (3)	27 (3)
F(3)	68 (2)	75 (3)	217 (5)	29 (2)	14 (3)	-4 (3)
F(4)	100 (3)	78 (3)	155 (4)	-5 (2)	37 (3)	27 (3)
F(5)	85 (3)	110 (3)	139 (4)	-11 (2)	59 (3)	-24 (3)
F(6)	95 (3)	170 (5)	100 (3)	-64 (3)	14 (2)	-44 (3)
O(1)	44 (2)	41 (2)	84 (3)	0 (2)	10 (2)	-5 (2)
O(2)	43 (2)	39 (2)	101 (3)	1 (2)	13 (2)	-5 (2)
N(1)	60 (3)	44 (3)	68 (3)	-8 (2)	5 (2)	0 (2)
N(2)	63 (3)	36 (2)	68 (3)	3 (2)	7 (2)	-4 (2)
C(1)	59 (4)	76 (5)	81 (4)	-4 (3)	24 (3)	-11 (4)
C(2)	51 (3)	53 (3)	54 (3)	5 (3)	0 (2)	-6 (3)
C(3)	62 (4)	56 (3)	65 (4)	11 (3)	13 (3)	-5 (3)
C(4)	70 (4)	48 (3)	58 (4)	15 (3)	1 (3)	-10 (3)
C(5)	99 (5)	48 (4)	107 (5)	26 (3)	14 (4)	-14 (3)
C(6)	63 (4)	78 (5)	124 (6)	-21 (4)	24 (4)	14 (4)
C(7)	58 (4)	56 (4)	60 (4)	-7 (3)	3 (3)	4 (3)
C(8)	45 (3)	57 (3)	85 (4)	1 (3)	5 (3)	1 (3)
C(9)	53 (3)	49 (3)	71 (4)	5 (3)	0 (3)	-1 (3)
C(10)	63 (4)	46 (3)	119 (6)	9 (3)	10 (4)	-2 (4)
C(11)	91 (5)	33 (3)	157 (7)	-7 (3)	23 (5)	0 (4)
C(12)	93 (5)	43 (4)	120 (6)	-7 (3)	37 (4)	11 (4)

^a The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The isotropic thermal parameters (B) for H(1)-H(6) are all 0.051 Å². ^b Anisotropic thermal parameters for Ni are $\times 10^4$.

Table III. Internuclear Distances (Å) in Ni[en(tfacac)₂]

Ni-O(1)	1.839 (4)	N(1)-C(12)	1.465 (7)
Ni-O(2)	1.848 (4)	N(2)-C(4)	1.303 (7)
Ni-N(1)	1.856 (4)	N(2)-C(11)	1.435 (7)
Ni-N(2)	1.864 (5)	C(1)-C(2)	1.539 (8)
F(1)-C(10)	1.313 (8)	C(2)-C(3)	1.330 (7)
F(2)-C(10)	1.315 (8)	C(3)-C(4)	1.429 (8)
F(3)-C(10)	1.306 (7)	C(4)-C(5)	1.526 (8)
F(4)-C(1)	1.319 (8)	C(6)-C(7)	1.524 (8)
F(5)-C(1)	1.319 (6)	C(7)-C(8)	1.431 (8)
F(6)-C(1)	1.311 (7)	C(8)-C(9)	1.356 (7)
O(1)-C(2)	1.283 (6)	C(9)-C(10)	1.515 (8)
O(2)-C(9)	1.274 (7)	C(11)-C(12)	1.412 (9)
N(1)-C(7)	1.299 (7)		

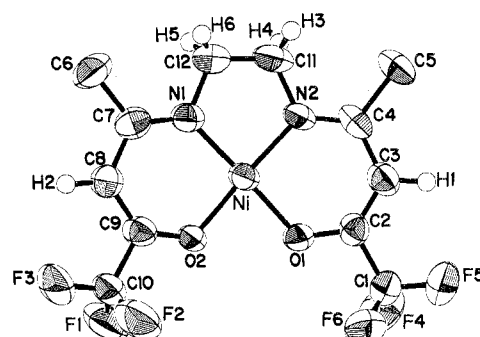


Figure 1. View of a single molecule of Ni[en(tfacac)₂], showing the atomic numbering scheme. The methyl hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are shown as spheres of arbitrary size.

arranged, but the condensation had occurred at the 4 position in both cases. The geometry and numbering scheme for the complex is shown in Figure 1; bond lengths and angles are given in Tables III and IV, respectively.

The average Ni-O and Ni-N distances of 1.844 (4) and 1.860 (5) Å are slightly shorter than the ranges of 1.85-1.93 and 1.89-2.01 Å, respectively, normally observed for square-planar nickel(II) complexes.¹⁷ The bond lengths and angles in the macrocycle are comparable to those found in similar complexes¹⁸⁻²⁰ where the ligand was en(acac)₂ and

Table IV. Intramolecular Angles (deg) in Ni[en(tfacac)₂]

O(1)-Ni-N(2)	95.0 (2)	C(1)-C(2)-C(3)	120.3 (5)
O(1)-Ni-O(2)	83.4 (2)	C(1)-C(2)-O(1)	111.4 (5)
O(1)-Ni-N(1)	177.9 (5)	C(2)-C(3)-C(4)	123.6 (5)
O(2)-Ni-N(1)	94.5 (2)	C(3)-C(4)-C(5)	117.0 (5)
O(2)-Ni-N(2)	177.2 (2)	C(5)-C(4)-N(2)	121.8 (6)
N(1)-Ni-N(2)	87.0 (2)	C(3)-C(4)-C(5)	121.2 (5)
Ni-O(1)-C(2)	124.0 (3)	N(1)-C(7)-C(8)	121.6 (5)
Ni-O(2)-C(9)	124.4 (4)	N(1)-C(7)-C(6)	121.6 (5)
Ni-N(1)-C(7)	127.7 (4)	C(6)-C(7)-C(8)	116.8 (5)
Ni-N(1)-C(12)	112.6 (4)	C(7)-C(8)-C(9)	122.5 (5)
Ni-N(2)-C(4)	126.9 (4)	C(8)-C(9)-O(2)	128.5 (5)
Ni-N(2)-C(11)	113.0 (4)	C(8)-C(9)-C(10)	118.7 (5)
F(4)-C(1)-F(5)	107.0 (6)	O(2)-C(9)-C(10)	112.8 (5)
F(4)-C(1)-F(6)	107.0 (6)	F(1)-C(10)-F(2)	106.0 (6)
F(5)-C(1)-F(6)	106.1 (5)	F(1)-C(10)-F(3)	106.6 (6)
O(1)-C(2)-C(3)	128.3 (5)	F(2)-C(10)-F(3)	107.2 (6)

where comparisons are possible to the only other reported nickel tetradentate Schiff base complex, Ni(salen).² Thus, it is characteristic that the C-C separation adjacent to the C-N bond be somewhat longer than the C-C distance adjacent to the C-O bond since the latter is formally a double bond. Normally it is also found that the C-C bond in the bridging ethylene is shortened from the value usually observed for simple ethylenediamine complexes; the value of 1.412 (9) Å reported here is the shortest yet observed.²¹ It is noteworthy that all chemically equivalent bond lengths in the structure are in excellent agreement, with the possible exception of the N(2)-C(11), N(1)-C(12) pair which differ by slightly more than 4σ. The six independent C-F distances in the CF₃ groups lie in the range 1.306 (7)-1.319 (8) Å, with an average value of 1.314 (5) Å. These values are similar to those found in other trifluoromethyl complexes^{22,24} and in the trifluoroacetate ion.^{25,26} The four ligating atoms are approximately coplanar, the average displacement from the best least-squares plane being 0.015 Å, and the nickel atom is essentially in this plane, its displacement being 0.023 Å. The bridging ethylene carbon atoms found here in the eclipsed conformation are displaced to the same side of the coordination plane as the nickel, while all other carbon atoms are displaced to the opposite side. The four atoms defining the ethylenediimine plane are displaced from this plane by an average of 0.018 Å, and the ethylenediimine plane makes an angle of 5.6° with the coordination plane. As a consequence of this, the two bridging carbon atoms cannot be displaced equally from the coordination plane, their displacements being 0.15 and 0.107 Å for C(11) and C(12), respectively. The results of various least-squares plane calculations are collected in Table V. It is apparent that the two chelate planes defined in Table V are very good, but the macrocycle as a whole is decidedly folded, the angle between the two chelates being 17.4°. This folding can be described in terms of two separate distortions: a rotation or twisting of the two chelates about their respective Ni-(γ carbon) vectors (Ni-C(3) for plane II, Ni-C(8) for plane III), followed by a fold along the line bisecting the N(1)-Ni-N(2) (or O(1)-Ni-O(2)) angle. The latter distortion is not quite symmetrical as evidenced by the unequal displacements of the γ carbons from the coordination plane (see Table V). The line of fold for the macrocycle is approximately along the Ni-O(2) (or Ni-N(2)) vector, indicating a nearly equal tendency to distort in both manners described above; this was also found to be the case for Ni(salen).² Distortions of this kind are common in structures of this type,^{19,20,27} but it has been suggested¹⁹ that too large a twisting or tetrahedral distortion would make it necessary for the ethylene bridge to assume the gauche conformation, and this contention is in fact supported by the structure data for Fe(salen).²⁷ In the present case, however, the tetrahedral distortion is considerably smaller than that in Fe(salen) as indicated by comparing the relative displacements of the constituent atoms from the least-squares

Table V

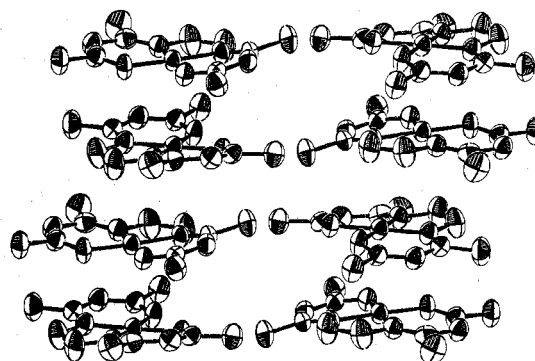
(A) Equations of Selected Planes in Orthogonal Coordinate System

Matrix Equation for Transformation from Crystal (x, y, z) to Orthogonal (X, Y, Z) System

$$\begin{pmatrix} a & 0 & c \cos \beta \\ 0 & b & 0 \\ 0 & 0 & c \sin \beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

(I) Coordination plane {O(1), O(2), N(1), N(2)}: $-0.1861X + 0.0232Y - 0.9822Z = 2.223$ (II) Chelate plane {O(1), N(2), C(2), C(3), C(4)}: $-0.3345X + 0.0882Y - 0.9383Z = 2.504$ (III) Chelate plane {O(2), N(1), C(7), C(8), C(9)}: $-0.0662X - 0.0394Y - 0.9970Z = 1.571$ (B) Displacements from Planes (Å)^a

	Plane I	Plane II	Plane III
Ni	-0.0229	0.1881	0.1452
O(1)	-0.0157*	0.0089*	0.2879
O(2)	0.0157*	0.4487	-0.0101*
N(1)	-0.0150*	0.3934	0.0078*
N(2)	0.0151*	-0.0041*	0.3814
C(1)	0.1795	-0.1170	0.7252
C(2)	0.1752	-0.0147*	0.6492
C(3)	0.3279	0.0092*	0.9141
C(4)	0.2342	0.0006*	0.7672
C(5)	0.4435	0.0397	1.1218
C(6)	0.2087	0.9677	-0.0441
C(7)	0.1463	0.7680	-0.0071*
C(8)	0.2599	0.9993	-0.0038*
C(9)	0.2051	0.8420	0.0131*
C(10)	0.3570	1.1318	0.0373
C(11)	-0.1544	-0.0938	0.1648
C(12)	-0.1072	0.1876	0.0228

^a Asterisks indicate atoms used in definition of least-squares planes.Figure 2. View of the crystal packing in Ni[en(tfacac)₂]. Fluorine and hydrogen atoms have been omitted for clarity.

planes, and, therefore, in the present case the folding distortion along the bisector of the N(1)-Ni-N(2) angle is probably great enough to assume the observed (eclipsed) conformation.

As is shown in Figure 2, the complexes are packed such that they form infinite chains, which is in contrast to the Ni(salen)² complex where the packing is best described in terms of isolated dimers. The complexes within the chain are spaced nearly equally, the two independent Ni-Ni distances in the chain being 4.024 (3) Å. Although all coordination planes are not crystallographically constrained to be parallel, they are nearly so, the angle between nonequivalent planes being 2.8°. This, of course, explains the observation by Lancione and Allen⁴ that the EPR spectra of Cu[en(tfacac)₂] doped in this lattice admit only one magnetic site for all orientations of the crystal with respect to the magnetic field. Also, one would expect that the z component of the g tensor for the copper atoms in this lattice will have the same direction cosines

with respect to the crystal axes as the perpendicular to the coordination plane, and this also was found to be the case.⁴

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Registry No. Ni[en(tfacac)₂], 40792-92-5.

Supplementary Material Available: listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Niobium Pentamethoxide— a Structure with Two Different Conformers in the Unit Cell

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Nb(OCH₃)₅ crystallizes in the triclinic system with $a = 8.684$ (3) Å, $b = 9.673$ (3) Å, $c = 12.543$ (3) Å, $\alpha = 69.33$ (2)°, $\beta = 85.84$ (2)°, and $\gamma = 86.46$ (3)° and with 4 formula units per unit cell, space group $P\bar{1}$. The structure was refined to $R = 0.04$; the esd's of the distances Nb–O and O–C are 0.007 and 0.01 Å and those of the bond angles O–Nb–O and Nb–O–C are 0.3 and 0.7°, respectively. The unit cell is pronouncedly pseudo body centered and contains two crystallographically different centrosymmetric dimeric molecules which have different conformations. Both forms consist of two approximately octahedral units with a shared edge, differentiated by a cis or trans arrangement of the equatorial methyl groups with respect to the equatorial plane. The evidence for a π contribution to the Nb–O bond and the absence of any significant trans effect is discussed.

Introduction

The preparation and solution properties of numerous transition metal alkoxides have been the subject of many publications and reviews.² By contrast there are very few data concerning their structures in the solid state. To our knowledge, the only x-ray structure determinations reported to date are those of the polymeric vanadium oxyalkoxide (VO(OCH₃)₃)_n³ and the tetrameric titanium alkoxides Ti₄(OCH₃)₁₆,⁴ Ti₄(OC₂H₅)₁₆,⁵ and Ti₄(OCH₃)₄(OC₂H₅)₁₂.⁶

In the case of the vanadium and the methoxy titanium compounds, the precision of the structures which were determined from film data ($R = 0.17$ and 0.14 , respectively) does not allow one to discuss the bonding parameters with any certainty; in the latter molecule two of the methoxy groups were presumed to be largely hydrolyzed in the sample which was analyzed. In the other two titanium alkoxides, only the metal and oxygen coordinates were reported.

This lack of existing data may well be attributable to the difficulty in obtaining suitable good-quality crystals for an x-ray study due to the extreme air sensitivity of these compounds.

The coordination chemistry,⁷ stereolability,⁸ and solvation⁹ of niobium pentamethoxide Nb(OCH₃)₅ have been extensively studied. The compound was found to be dimeric in nonpolar

solvents^{8a,b} and in noncomplexing polar solvents.^{8d} The dimeric unit has been shown to be retained in the vapor phase by mass spectrometry.¹⁰ A precise knowledge of its molecular structure was expected to shed some light on its solvation properties, structural dynamics, and chemical behavior and also on the question of a trans effect, or inequivalence in d_{π} - p_{π} contribution between the axial and equatorial metal-oxygen bonds.

The crystal and molecular structure of Nb(OCH₃)₅ is reported herein. It presents the interesting feature of the existence of two conformers of the same molecule in the unit cell.

Experimental Section

Niobium pentamethoxide¹¹ readily forms monocrystals by slow sublimation when stored at 47 °C in an evacuated tube. However, the transfer of these extremely air-sensitive crystals to Lindemann tubes proved impossible with the equipment at our disposal. Suitable crystals were therefore prepared in the following manner. The alkoxide (~50 mg) was sealed into an evacuated 0.5-ml Pyrex glass ampule with one end drawn out into a fine capillary. The ampule was kept at 47 ± 0.5 °C for 4 weeks. After this time, several suitable crystals had formed in the capillary which was then sealed off from the ampule. In this manner, we were able to store the crystals in vacuo and without change for many weeks at room temperature. The rather thick walls of the capillary, however, led to a higher background of the x-ray intensities than normal, especially for the low-order reflections.