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Crystal and Molecular Structure and Isotropic Hydrogen-1 Nuclear Magnetic Resonance Shifts of Hexa(acetic acid)nickel(II) Tetrafluoroborate, $[Ni(AcOH)_6](BF_4)_2$[1]

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The crystal structure of hexa(acetic acid)nickel(II) tetrafluoroborate has been determined and the structure of the coordinated acetic acid is compared with the structure of free acetic acid and with the coordinated acetate ion of bis(acetato)tetraaquonickel(II). The crystals of $[Ni(AcOH)_6](BF_4)_2$ are triclinic belonging to space group $P\bar{1}$ with $a = 10.092$ (2) Å, $b = 8.706$ (2) Å, $c = 9.147$ (2) Å, $\alpha = 112.29$ (2)°, $\beta = 97.81$ (2)°, and $\gamma = 115.34$ (2)° at 20°, with one molecule per unit cell. All unique reflections for which $2\theta < 50°$ were measured using graphite-monochromatized Mo $K\alpha$ radiation with a pulse height analyzer. The structure was refined by large block diagonal least-squares methods using 1764 reflections to a final R index of 0.058. The acetic acid is coordinated to the Ni(II) ion through the carbonyl oxygen with an average bond length of 2.055 (4) Å, which is slightly shorter than the Ni–O bond length of 2.068 (1) Å found for $Ni(H_2O)_4(AcO)_2$. Other changes in geometry of the acetic acid upon coordination are barely significant. The hydroxyl hydrogen of the acetic acid is involved in a bifurcated hydrogen bond to the carbonyl group of the same acid and to a fluorine of the BF_4^- anion. The isotropic ^1H NMR shifts determined from magnetic dilution experiments for the methyl and hydroxyl protons are −4.33 and −2.49 ppm, respectively. When compared to the contact shifts determined from a neat solution of $[Ni(AcOH)_6](BF_4)_2$, these results indicate some dissociation of the complex in solution.

Introduction

Recently Van Leeuwen[2] reported both the synthesis and spectral properties of a new series of compounds which contained six acetic acid groups coordinated to the divalent cations of Mg, Mn, Co, Ni, Cu, and Zn and with the tetrafluoroborate, perchlorate, and nitrate counteranions. In an effort to continue our investigations into both the structural and bonding characteristics of similar complexes of protonated ligands,[3,4] we have determined the structure of hexa(acetic acid)nickel(II) tetrafluoroborate, $[Ni(AcOH)_6](BF_4)_2$, by crystallographic techniques.

In order to compare accurately the structural differences of a coordinated carboxylic acid with that of the corresponding conjugate base, a coordinated carboxyl anion, we repeated independently the structure of bis(acetato)tetraaquonickel(II) $[Ni(H_2O)_4(AcO)_2]$ first reported by Van Niekerk and Schoening[5] in 1953 and again by Raper[6] et al. in 1971. In order to compare reliably the two structures the intensity data for both compounds were collected and analyzed under identical conditions using the same statistical and least-squares methods.

In an effort to determine whether the structure of the molecule was maintained in solution we have determined the ^1H NMR isotropic shifts.

Experimental Section

Synthesis of $[Ni(AcOH)_6](BF_4)_2$ was accomplished by the method of Van Leeuwen.[2] $Ni(H_2O)_4(AcO)_2$ was obtained commercially and purified by recrystallization from a 50:50 v/v solution of water and ethanol.

Collection and Reduction of Intensity Data

Light green crystals of $[Ni(AcOH)_6](BF_4)_2$ were grown by slow cooling over a 4-day period from a solution of the salt in dried glacial acetic acid, nearly saturated at 60°. A single crystal, of space group $P\bar{1}$, irregularly shaped with maximum dimensions of 0.030 × 0.040 × 0.060 cm, was selected and was lodged and sealed in a thin-walled capillary tube. A volume of mother liquor approximately equal to that of the crystal was included in such a way that the crystal was entirely bathed in liquid throughout data collection. The crystal of $Ni(H_2O)_4(AcO)_2$ was monoclinic, space group $P2_1/c$, with maximum dimensions of 0.034 × 0.016 × 0.016 cm.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, λ 0.70926 Å; $K\alpha_2$, λ 0.71354 Å) and with a pulse height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants were determined by least-squares methods from the centered angular coordinates of 15 intense reflections. The cell constants at 20° for $[Ni(AcOH)_6](BF_4)_2$ are $a = 10.092$ (2) Å, $b = 8.706$ (2) Å, $c = 9.147$ (a) Å, $\alpha = 112.29$ (2)°, $\beta = 97.81$ (2)°, and $\gamma = 115.34$ (2)°; $V = 627.9$ (2) Å^3 and $\rho_{calcd} = 1.567$ g/cm^3. The density was not successfully measured by flotation because of the instability of the complex. The cell constants for $Ni(H_2O)_4(AcO)_2$ were obtained similarly and at 20° were found to be $a = 4.760$ (1) Å, $b = 11.761$ (4) Å, $c = 8.419$ (4) Å, and $\beta = 93.82$ (3)° with $V = 470.3$ (3) Å^3. The calculated density $\rho_{calcd} = 1.75$ g/cm^3 agrees with the measured density of $\rho_{measd} = 1.78$ g/cm^3.

Diffraction intensities were collected by the θ–2θ scan technique at a minimum scan rate of 3°/min in 2θ to 24°/min in such a way

Table I. Final Nonhydrogen Positional Parameters and Anisotropic Thermal Parameters and Their Standard Deviations for $[\mathrm{Ni(AcOH)_6}](\mathrm{BF_4})_2$[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0000 (0)	0000 (0)	0000 (0)	76 (1)	171 (2)	97 (1)	106 (2)	59 (2)	76 (2)
F(1)	8114 (6)	4957 (11)	1288 (8)	254 (8)	734 (23)	355 (12)	549 (24)	252 (17)	187 (27)
F(2)	5797 (5)	4405 (9)	1228 (7)	160 (6)	569 (17)	337 (11)	316 (17)	−60 (13)	−35 (22)
F(3)	7279 (20)	3901 (26)	2837 (28)	722 (40)	1190 (68)	1217 (74)	842 (87)	432 (86)	1950 (134)
F(4)	7903 (7)	6916 (9)	3430 (7)	306 (9)	517 (16)	263 (9)	478 (21)	−1 (15)	−102 (20)
O(1)	1471 (3)	0757 (5)	2272 (4)	108 (4)	248 (8)	123 (5)	170 (9)	62 (7)	115 (10)
O(2)	3323 (5)	1490 (8)	4432 (5)	203 (7)	459 (14)	148 (6)	394 (17)	41 (10)	164 (15)
O(3)	0302 (3)	2732 (4)	1016 (4)	102 (4)	183 (7)	147 (5)	120 (9)	80 (7)	75 (10)
O(4)	1062 (4)	5839 (5)	2310 (6)	156 (5)	186 (8)	282 (9)	168 (11)	133 (11)	78 (13)
O(5)	−1899 (3)	−0942 (4)	0721 (4)	97 (4)	222 (7)	132 (5)	129 (9)	96 (7)	113 (10)
O(6)	−3746 (4)	−1353 (6)	1820 (5)	126 (5)	334 (10)	192 (7)	178 (11)	174 (9)	175 (13)
C(1)	2609 (5)	0697 (6)	2808 (6)	112 (6)	202 (10)	140 (7)	130 (12)	63 (10)	134 (13)
C(2)	3336 (7)	−0228 (9)	1770 (8)	182 (8)	338 (15)	219 (10)	344 (19)	169 (15)	241 (20)
C(3)	1360 (5)	4425 (7)	1891 (6)	121 (6)	199 (10)	138 (7)	144 (13)	102 (10)	105 (14)
C(4)	3050 (6)	5133 (8)	2580 (9)	116 (6)	229 (12)	265 (12)	93 (14)	50 (14)	122 (10)
C(5)	−2286 (5)	−0392 (7)	1933 (6)	124 (6)	239 (10)	141 (7)	196 (13)	133 (11)	164 (14)
C(6)	−1244 (7)	1329 (9)	3604 (7)	177 (8)	327 (15)	157 (8)	189 (18)	158 (14)	90 (19)
B(1)	7209 (7)	5002 (10)	2272 (8)	148 (8)	282 (14)	185 (10)	237 (18)	98 (15)	152 (20)

[a] Values are given × 10^4. See Figure 1 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

that more time was spent on weaker reflections to improve their standard deviations. Most reflections were observed at the slowest scan rate. All 2225 and 873 unique reciprocal lattice points for which $2\theta < 50°$ were examined for $[\mathrm{Ni(AcOH)_6}](\mathrm{BF_4})_2$ and $\mathrm{Ni(H_2O)_4(AcO)_2}$ respectively.

A time equal to half the scan time for each reflection was spent counting the background at each end of the scan range. A set of check reflections was measured periodically during data collection for both data sets and for the $[\mathrm{Ni(AcOH)_6}](\mathrm{BF_4})_2$ the average total decrease in intensity was 10% while for $\mathrm{Ni(H_2O)_4(AcO)_2}$ the check reflections showed no decrease in intensity. The appropriate decay correction was performed for the $[\mathrm{Ni(AcOH)_6}](\mathrm{BF_4})_2$ data set. Absorption corrections for both data sets were performed using the cartesian coordinates of each crystal face and the compound's linear absorption coefficient. The linear absorption coefficient for $[\mathrm{Ni(AcOH)_6}](\mathrm{BF_4})_2$ was calculated to be 8.91 $\mathrm{cm^{-1}}$ while for $\mathrm{Ni(H_2O)_4(AcO)_2}$ a value of 20.75 $\mathrm{cm^{-1}}$ was calculated. Transmission coefficients ranged from 0.7054 to 0.7922 for $[\mathrm{Ni(AcOH)_6}](\mathrm{BF_4})_2$ and from 0.6849 to 0.7758 for $\mathrm{Ni(H_2O)_4(AcO)_2}$.

Standard deviations were assigned according to the formula

$$\delta(I) = [w^2(\mathrm{CT}) + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated count obtained in a scan time of t_c, B_1 and B_2 are the background counts each obtained in time t_b, and $I = w[\mathrm{CT} - 0.5(t_c/t_b)(B_1 + B_2)]$. A value of 0.02 was assigned to the empirical parameter p to account for instrument instability. The net counts were then corrected for Lorentz and polarization effects.

The principal programs used in this study were as follows: LPCOR data reduction program, A. Christensen, Syntex Analytical Instruments, 1970; ABSCO absorption correction program for crystals of essentially arbitrary shape, based on ABCO, T. Dahl, Chemistry Department, University of Oslo, Oslo, Norway, modification for use at the University of Hawaii by T. Ottersen and K. Seff; FMLS full-matrix least squares, P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLALS4, American Crystallographic Association Program Library (old) No. 317 (modified); FFOUR Fourier program, C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, Ames Laboratory Fast Fourier, Iowa State University, 1971; C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Atomic scattering factors for $\mathrm{Ni^{2+}}$, $\mathrm{O^0}$, $\mathrm{C^0}$, $\mathrm{F^-}$, and $\mathrm{B^{3+}}$ (valence[7]) and H (bonded[8]) were used.

Solution and Refinement of $[\mathrm{Ni(AcOH)_6}](\mathrm{BF_4})_2$

The positions of two oxygen atoms, one fluorine, and the nickel ion were determined from a three-dimensional Patterson function. Successive cycles of Fourier refinement with phases based initially on the four atoms found in the Patterson analysis revealed the location of the remaining nonhydrogen atoms of the molecule. Full-matrix least-squares refinement with isotropic thermal parameters for all nonhydrogen atoms within the molecule converged at $R_1 = 0.1504$ and $R_2 = 0.1708$. Full-matrix least-squares anisotropic refinement of all nonhydrogen positions gave $R_1 = 0.063$ and $R_2 = 0.066$. At this point a difference Fourier synthesis revealed the three hydroxy protons and at least one methyl hydrogen for each methyl group. The methyl hydrogen coordinates were then calculated[9] assuming tetrahedral geometry and 1.08-Å bond lengths. The methyl hydrogens were given isotropic temperature factors of 10.00 and the hydroxy protons were refined isotropically using full-matrix least-squares techniques. Finally all atomic positions were included and the nonhydrogen positions were allowed to refine for three more cycles. The final calculation of the structure factors and error functions yielded $R_1 = 0.058$ and $R_2 = 0.062$. The "goodness of fit", $\{[\sum w(F_o - |F_c|)^2]/(m - s)\}^{1/2}$, is 1.68. The number of reflections (1764) is m, while s (163) is the total number of variables in the least-squares calculations. The estimated standard deviation of the electron density in the final Fourier function was 0.104 e/Å^3 with difference peaks as large as 1.0 around the fluorines and especially $\mathrm{F_3}$ which has the largest thermal parameters.

Table II. Hydrogen Atom Positions and Assigned Thermal Parameters for $[\mathrm{Ni(AcOH)_6}](\mathrm{BF_4})_2$[a]

	x	y	z	B, Å^2
H(1)	2865	1964	4746	13.5
H(2)	4475	0920	1975	10.0
H(3)*	3367	−1261	2132	10.0
H(4)*	2458	−1280	0519	10.0
H(5)	0050	4712	1706	6.4
H(6)	3240	3997	1779	10.0
H(7)*	3729	6508	2672	10.0
H(8)*	3318	5400	3885	10.0
H(9)	−4257	−2443	0786	6.1
H(10)	−0057	1674	3742	10.0
H(11)*	−1653	0982	4533	10.0
H(12)*	−1545	2413	3722	10.0

[a] Fractional coordinates × 10^4 are given. Atoms whose positions were calculated are indicated by an asterisk.

$$R_1 = (\Sigma|F_o - |F_c||)/\Sigma F_o$$

$$R_2 = (\Sigma w(F_o - |F_c|)^2/\Sigma w F_o^2)^{1/2}$$

A listing of observed and calculated structure factors is available.[10] Tables I and II give the positional and thermal parameters of $[\mathrm{Ni(AcOH)_6}](\mathrm{BF_4})_2$ and their standard deviations. Bond lengths and angles and their standard deviations are given in Table III.

Solution and Refinement of $\mathrm{Ni(H_2O)_4(AcO)_2}$

The earlier structural study of Van Niekerk and Schoening[5] gave a set of fractional coordinates with which full-matrix least-squares refinement was begun. Isotropic refinement of all nonhydrogen positions gave $R_1 = 0.07982$ and $R_2 = 0.1036$. Anisotropic refinement of all nonhydrogen positions gave $R_1 = 0.03991$ and $R_2 = 0.4006$. At this point all hydrogen positions were obtained from a difference Fourier synthesis. These hydrogen positions were then isotropically

Table III. Bond Distances (Å) and Angles (deg) and Standard Deviations for $[Ni(AcOH)_6](BF_4)_2$

Cation Distances

Ni–O(1)	2.060 (3)	O(2)–H(1)	0.759 (9)
Ni–O(3)	2.059 (5)	O(4)–H(5)	0.943 (9)
Ni–O(5)	2.047 (3)	O(6)–H(9)	0.910 (9)
O(1)–C(1)	1.216 (4)	O(2)–H(2)	1.082 (10)
O(3)–C(3)	1.216 (7)	C(2)–H(3)	1.080 (10)
O(5)–C(5)	1.218 (5)	C(2)–H(4)	1.081 (10)
C(1)–O(2)	1.307 (6)	C(4)–H(6)	1.097 (9)
C(3)–O(4)	1.321 (6)	C(4)–H(7)	1.055 (9)
C(5)–O(6)	1.311 (6)	C(4)–H(8)	1.096 (11)
C(1)–C(2)	1.485 (8)	C(6)–H(10)	1.078 (10)
C(3)–C(4)	1.482 (7)	C(6)–H(11)	1.078 (10)
C(5)–C(6)	1.471 (8)	C(6)–H(12)	1.083 (10)

Cation Angles

O(1)–Ni–O(3)	90.37 (0.9)	O(6)–C(5)–C(6)	113.7 (0.4)
O(3)–Ni–O(5)	89.36 (0.9)	C(1)–O(2)–H(1)	98.4 (0.8)
O(1)–Ni–O(5)	90.85 (0.8)	C(3)–O(4)–H(5)	77.5 (0.6)
Ni–O(1)–C(1)	139.2 (0.2)	C(5)–O(6)–H(9)	106.3 (0.7)
Ni–O(3)–C(3)	138.8 (0.3)	C(1)–O(2)–H(2)	107.7 (0.6)
Ni–O(5)–C(5)	139.3 (0.3)	C(1)–C(2)–H(3)	107.2 (0.7)
O(1)–C(1)–O(2)	121.0 (0.3)	C(1)–C(2)–H(4)	107.2 (0.6)
O(3)–C(3)–O(4)	120.5 (0.4)	C(3)–C(4)–H(6)	107.5 (0.6)
O(5)–C(5)–O(6)	120.4 (0.4)	C(3)–C(4)–H(7)	109.5 (0.7)
O(1)–C(1)–C(2)	126.9 (0.3)	C(3)–C(4)–H(8)	107.2 (0.6)
O(3)–C(3)–C(4)	126.1 (0.5)	C(5)–C(6)–H(10)	107.9 (0.7)
O(5)–C(5)–C(6)	125.9 (0.4)	C(5)–C(6)–H(11)	107.2 (0.6)
O(2)–C(1)–C(2)	113.0 (0.5)	C(5)–C(6)–H(12)	107.1 (0.6)
O(4)–C(3)–C(4)	113.4 (0.4)		

Tetrafluoroborate Anion Distances

B(1)–F(1)	1.369 (9)	B(1)–F(3)	1.272 (20)
B(1)–F(2)	1.354 (8)	B(1)–F(4)	1.360 (9)

Tetrafluoroborate Anion Angles

F(1)–B(1)–F(2)	105.3 (0.6)	F(4)–B(1)–F(1)	104.9 (0.5)
F(2)–B(1)–F(3)	117.8 (0.9)	F(1)–B(1)–F(3)	102.0 (0.9)
F(3)–B(1)–B(4)	116.2 (1.0)	F(2)–B(1)–F(4)	108.9 (0.5)

refined along with the nonhydrogen positions to final *R* indexes of $R_1 = 0.02866$ and $R_2 = 0.02842$. The goodness of fit was 1.207. The estimated standard deviation of the electron density of the final Fourier function was found to be 0.121 e Å^3. A listing of observed and calculated structure factors is available.[10]

Table IV gives the final positional and thermal parameters for both hydrogen and nonhydrogen positions in $Ni(H_2O)_4(AcO)_2$ while Table V lists bond angles and distances. The numbering system used in this work is in accord with those previously published.

In both structures the final cycle of least-squares refinement yielded shifts that were less than their standard deviations.

The asymmetric unit for $[Ni(AcOH)_6](BF_4)_2$ is shown in Figure 1. Figure 2 presents the entire molecule without the methyl hydrogens in stereoview produced by ORTEP, while Figure 3 is the crystal packing diagram in stereoview.

NMR Isotropic Shifts

The ^1H NMR isotropic shifts were measured relative to the corresponding Zn^{2+} complex using either an HA-100 or XL-100 FT instrument, by two different techniques. In one case the spectrum of $Ni(AcOH)_6^{2+}$ in CD_3NO_2 was recorded directly while the second method involved dilution with known amounts of Zn^{2+} complex. The data from the dilution experiments were then plotted as previously described[11] to obtain the isotropic shifts of $Ni(AcOH)_6^{2+}$.

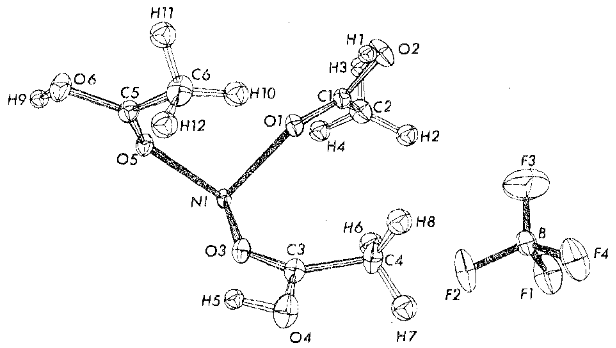

Figure 1. View of an asymmetric unit of $[Ni(AcOH)_6](BF_4)_2$ showing the 50% probability ellipsoids and the atomic numbering scheme. The hydrogen thermal parameters have been constrained for clarity.

Description and Discussion of Structure

In both $[Ni(AcOH)_6](BF_4)_2$ and $Ni(H_2O)_4(AcO)_2$ the nickel ions are surrounded by an octahedral arrangement of oxygen atoms. Because the nickel ion occupies a center of symmetry at 0, 0, 0 in both structures the octahedron is formed by three symmetry-related pairs of oxygen atoms. In both structures the angles within the octahedron are 90° within experimental error, Tables III and V, but in $Ni(H_2O)_4(AcO)_2$ the nickel–oxygen distances are significantly different from one another and thus the octahedron must be regarded as being slightly distorted. Sacconi[12] has pointed out that distortions in octahedral nickel complexes, where the nickel ion is bonded to the same type of atom, must be due to steric factors and the requirements of crystal packing.

Table VI summarizes the structural results of this as well as other selected crystallographic studies involving the carboxyl group or ion. Examination of Table VI reveals that the metal–oxygen bonding in the hexa(acetic acid) complex occurs at the carbonyl oxygen, a result predicted by Van Leeuwen[2] spectroscopically. A similar examination of nickel acetate, however, reveals that the nickel ion replaces the hydroxyl proton and does not bind to the carbonyl group. The acetate structure is therefore similar to other structures containing carboxylate anions[13,14] while the structure of $Ni(AcOH)_6^{2+}$ illustrates a new mode of metal ion bonding not observed before for carboxylic acids. The structure of $Ni(AcOH)_6^{2+}$ thus provides experimental confirmation for the coordination of acetic acid to Ni(II) as recently postulated by Hammond and Wu[15] as an intermediate in the autoxidation of benzoin using nickel acetate as a catalyst.

Further examination reveals that the nickel–oxygen bond

Table IV. Positional and Thermal Parameters and Their Standard Deviations for $Ni(H_2O)_4(AcO)_2$[a]

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0000 (0)	0000 (0)	0000 (0)	116 (2)	23 (0)	61 (1)	1 (1)	−55 (1)	4 (1)
O(1)	−2324 (3)	−1482 (1)	0086 (2)	153 (6)	28 (1)	101 (3)	−3 (4)	−68 (6)	10 (3)
O(2)	0709 (4)	−2565 (1)	1511 (3)	302 (8)	35 (1)	140 (3)	−8 (5)	−163 (8)	45 (3)
O(3)	−2763 (4)	0802 (1)	1459 (2)	153 (6)	34 (1)	82 (2)	15 (5)	−72 (6)	−16 (3)
O(4)	2368 (4)	−0462 (2)	2009 (2)	197 (8)	37 (1)	82 (2)	−18 (5)	−80 (6)	5 (3)
C(1)	−1416 (4)	−2448 (2)	0575 (3)	198 (9)	31 (2)	79 (3)	−3 (6)	8 (8)	10 (3)
C(2)	−2962 (9)	−3483 (2)	−0043 (4)	360 (12)	37 (2)	129 (5)	−58 (8)	−54 (12)	1 (5)

	x	*y*	*z*	*B*, Å^2		*x*	*y*	*z*	*B*, Å^2
H(1)	−466 (16)	−3450 (7)	80 (9)	8.1 (1.8)	H(5)	−388 (8)	114 (3)	104 (4)	2.1 (6)
H(2)	−239 (10)	−416 (5)	43 (7)	5.4 (1.0)	H(6)	222 (9)	−108 (5)	199 (6)	3.8 (9)
H(3)	−258 (14)	−350 (6)	−98 (10)	7.4 (1.6)	H(7)	392 (9)	−31 (3)	201 (4)	2.5 (6)
H(4)	−210 (8)	123 (3)	211 (5)	3.0 (7)					

[a] Values for nonhydrogen atoms are × 10^4. All values for hydrogen are × 10^3 except the isotropic thermal parameters. The esd is in the units of the least significant digit given for the corresponding parameter.

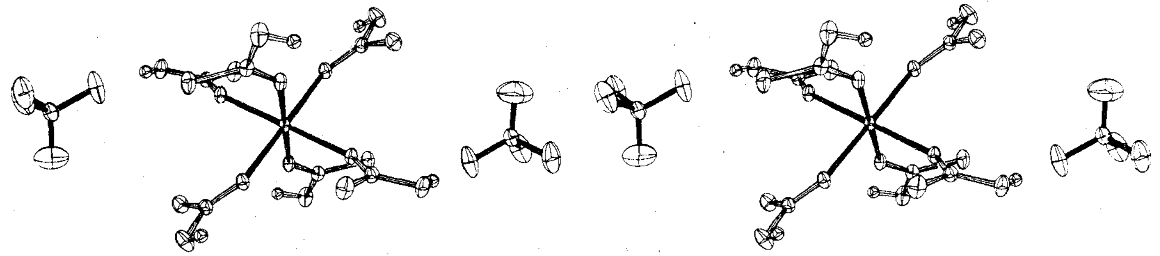

Figure 2. Stereoview of $[Ni(AcOH)_6](BF_4)_2$ showing the 50% probability ellipsoids. The methyl hydrogen atoms have been omitted for clarity.

Table V. Bond Distances (Å) and Angles (deg) and Their Standard Deviations for $Ni(H_2O)_4(AcO)_2$

	Distances		
Ni-O(1)	2.068 (1)	O(3)-H(2)	0.795 (41)
Ni-O(3)	2.084 (2)	O(4)-H(3)	0.734 (52)
Ni-O(4)	2.043 (2)	O(4)-H(4)	0.759 (42)
O(1)-C(1)	1.275 (3)	C(2)-H(5)	0.916 (55)
O(2)-C(1)	1.247 (3)	C(2)-H(6)	0.819 (84)
C(1)-C(2)	1.497 (4)	C(2)-H(7)	0.820 (77)
O(3)-H(1)	0.732 (36)		
	Angles		
Ni-O(1)-C(1)	126.3 (0.1)	O(1)-C(1)-O(2)	123.1 (0.2)
Ni-O(3)-H(1)	115.4 (2.8)	O(1)-C(1)-C(2)	117.6 (0.2)
Ni-O(3)-H(2)	117.3 (2.9)	O(2)-C(1)-C(2)	119.3 (0.2)
Ni-O(4)-H(3)	101.4 (3.4)	C(1)-C(2)-H(5)	115.3 (3.7)
Ni-O(4)-H(4)	114.6 (2.7)	C(1)-C(2)-H(6)	102.3 (5.4)
O(3)-Ni-O(4)	88.1 (0.1)	C(1)-C(2)-H(7)	112.4 (5.5)
O(1)-Ni-O(3)	90.0 (0.1)	H(1)-O(3)-H(2)	102.9 (4.0)
O(1)-Ni-O(4)	90.8 (0.1)	H(3)-O(4)-H(4)	108.8 (4.6)

in the acetic acid complex, when compared to the acetate structure, is shortened although the two values 2.055 (4) and 2.068 (1) Å border on the 3σ level of significance. This leads to the conclusion that there is little if any difference in the strengths of the nickel–ligand bonds in the two cases. This rather surprising conclusion implies that coordinated carboxylic acids may be more common in coordination chemistry than is generally believed. The failure to commonly observe coordinated carboxylic acids in aqueous solution cannot, therefore, be attributed to a weak metal–oxygen bond but may instead be due to other factors such as solvation.

Examination of the Ni–O–C angles within the two structures shows a significant expansion of this angle in the acetic acid complex—139.1 (0.3)° compared to 126.3 (0.1)° observed for the acetate structure. The difference in these angles probably results from the fact that the acetate ion is hydrogen bonded to an H_2O in the Ni(II) coordination sphere, while no such interaction occurs in $Ni(AcOH)_6^{2+}$.

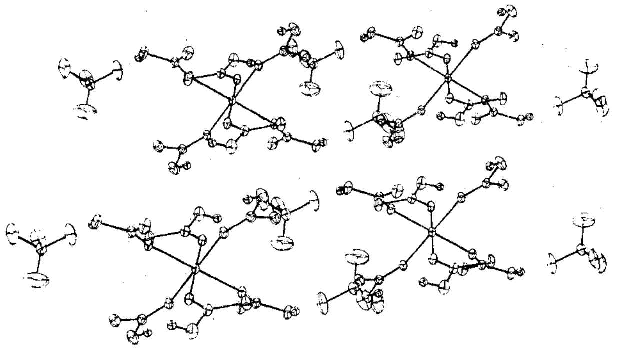

Figure 3. View of the packing diagram of $[Ni(AcOH)_6](BF_4)_2$ showing the 50% probability ellipsoids. The methyl hydrogen atoms have been removed for clarity.

It is of interest to compare the bonding observed in the acetic acid structure to that of other carboxylic acids not coordinated to a metal ion. Such a comparison is hampered by the lack of high-precision crystallographic results on carboxylic acids, since most workers[16-19] have reported bond lengths to ±0.02 Å and bond angles to ±1°. Fortunately, however, the structure of acetic acid has recently been reinvestigated by both crystallographic[20] and neutron diffraction[21] techniques and

Table VI. Comparison of Structural Results

Compd	Distances, Å C–C	C=O	C–O(H)	O=C–O(H)	O=C–C	(H)O–C–C	M–O	Ref
$[Ni(AcOH)_6](BF_4)_2$	1.479 (7)	1.217 (5)	1.313 (6)	120.6 (4)	126.0 (4)	113.4 (5)	2.055 (4)	This work
$Ni(H_2O)_4(AcO)_2$	1.497 (4)	1.247 (3)	1.275 (3)	123.1 (2)	119.3 (2)	117.6 (2)	2.068 (1)	This work
RCOOH[a]	1.53 (2)	1.24 (2)	1.33 (2)	122 (1)	123 (1)	115 (1)		15-18
AcOH, −190°	1.478 (6)	1.229 (5)	1.319 (6)	121.1 (5)	125.1 (5)	113.8 (3)		19
+5°	1.482 (8)	1.220 (6)	1.318 (2)	122.0 (6)	124.2 (7)	113.8 (4)		19
Neutron diffraction	1.501 (7)	1.206 (8)	1.321 (7)	121.9 (5)	124.9 (5)	113.2 (5)		20

[a] $R = CH_3, CH_3CH_2, CH_3(CH_2)_2, CH_3(CH_2)_3$.

Table VII. Deviations of Atoms from Least-Squares Planes (Å × 10^4)[a]

	$[Ni(AcOH)_6](BF_4)_2$						$Ni(H_2O)_4(AcO)_2$	
	Atoms	Plane 1	Atoms	Plane 2	Atoms	Plane 3	Atoms	Plane 1
	O(1)	1	O(3)	−7	O(5)	−1	O(1)	−11
	O(2)	2	O(4)	−2	O(6)	−2	O(2)	−19
	C(1)	−6	C(3)	13	C(5)	7	C(1)	73
	C(2)	3	C(4)	−4	C(6)	−4	C(2)	−43
	Ni	1239	Ni	227	Ni	−2100	Ni	−6819
	H(1)	733	H(5)	510	H(9)	880		
$q_b \times (a \times b)$		6304		−4341		1021		−6348
q_b		7757		−3681		−9482		459
$q_a \times b$		309		8222		3008		7713

[a] In each plane the four acetate atoms define the least-squares plane. A negative deviation from a plane indicates that the atom lies between the plane and the origin. The direction cosines (× 10^4), q, are with respect to orthogonal axes.

Table VIII. Hydrogen Bonds in $[Ni(AcOH)_6](BF_4)_2$

Atoms			Bonds, Å		Angles, deg	
B	H	A	B–H	H–A	BHB	BHA
O(1)			2.066			90
	H(1)	O(2)		0.759	117	
F(4′)[a]			2.025			150
O(3)			1.740			107
	H(5)	O(4)		0.943	133	
F(1)[b]			2.056			120
O(5)			2.193			78
	H(9)	O(6)		0.910	116	
F(2′)			1.814			160

[a] F(4′) is located in (111). [b] F(1) is located in (100).

these results are summarized in Table VI. *It is interesting that coordination of the carboxylic acid produces no significant structural change.*

Table VII summarizes the deviation observed for the atoms defining the least-squares planes in both structures. Both the acetate ion and the three acetic acid molecules are accurately planar, but the Ni(II) ions do not lie in these planes. The Ni(II) lies considerably further from the plane of the acetate, 0.682 Å, than it does in the case of the acetic acids, where the average deviation is 0.119 Å.

The geometry of $Ni(H_2O)_4(AcO)_2$, including the geometry of the acetate ions, is in complete agreement with the earlier determination of Raper,[6] the only difference being the somewhat lower standard deviations in our work. While the difference in the two carbon–oxygen bond lengths in Raper's work is barely significant at the 3σ level, 1.255 (5) vs. 1.272 (5) Å, this difference in our work is greater than 8σ, 1.247 (3) vs. 1.275 (3) Å. Since the z coordinate of C(1), 0.25834 Å, in the earlier work[6] is not in accord with the published bond distances or with our value of 0.0575 Å it appears to be a typographical error.

Hydrogen Bonding

Since both compounds are extensively hydrogen bonded, we will briefly discuss the hydrogen-bonding network of $[Ni(AcOH)_6](BF_4)_2$ and refer the reader to Raper et al.[6] for a discussion of the hydrogen-bonding network in $Ni(H_2O)_4(AcO)_2$.

The bond distances and angles of the hydrogen-bonding network are listed in Table VIII. Examination of the hydrogen-bonding network in the acetic acid complex reveals that each hydroxyl hydrogen is participating in a bifurcated hydrogen bond; i.e., each hydrogen is intramolecularly hydrogen bonded to the carbonyl oxygen while simultaneously being intermolecularly hydrogen bonded to a tetrafluoroborate fluorine. Both H(5) and H(9) refine to approximate isotropic temperature factors of 6.00 and can therefore be regarded as well defined. Both show bifurcated hydrogen bonds with the following bond distances in Å: O(5)–H(9), 2.193; F(2)–H(9), 1.814; O(3)–H(5), 1.740; F(1)–H(5), 2.055. H(1) which refines to an isotropic temperature factor of 13.5 exhibits a similar bifurcated hydrogen bond of 2.066 Å for O(1)–H(1) and 2.025 Å for F(4)–H(1). Examination of the O–H–O angles in Table VIII shows that they are quite small, which is to be expected when one considers the sp^2 hybridization of the carbon and oxygen atoms which along with the hydrogen form a ring. As a result the hydrogen is not symmetrically imbedded in the carbonyl lone pair but rather lies in its edge. The positive charge of the hydrogen is thus not perfectly screened inviting the attentions of the fluorine and resulting in a bifurcated hydrogen bond.

The geometry of the BF_4^- ion is similar to that usually observed. It is interesting to note that F(3) which does not participate in hydrogen bonding has the largest anisotropic temperature factors which produce an apparent short bond.

Solution Studies

A plot of equivalent conductance (Λ_{eq}) for $[Ni(AcOH)_6](BF_4)_2$ vs. $M^{1/2}$ results in a line with a slope of approximately 480, a value which lies in the range of values (392–510[22]) for a 1:2 electrolyte in CH_3NO_2 solution. This result suggests that no significant coordination of BF_4^- ions or dissociation of protons from acetic acid is taking place, although a minor contribution from these reactions would not be detected.

An earlier comparison of visible spectra in the solid state and in solution had led to the suggestion that $[Ni(AcOH)_6](ClO_4)_2$ would dissolve in CH_3NO_2 without dissociation.[2] The NMR results do not reinforce this suggestion. The shifts obtained for the pure complex in CH_3NO_2 solution for the CH_3 and OH functional groups are −3.72 and −1.88 ppm, respectively, while those obtained from the dilution experiments are −4.33 ± 0.03 and −2.49 ± 0.06 ppm. These results suggest that there is some dissociation of acetic acid from the Ni(II) ion in CH_3NO_2 solution.

The isotropic shift results also suggest that the AcOH ligand remains coordinated through the carbonyl group in solution. If the hydroxyl group became coordinated to the Ni^{2+} ion in solution, we would expect its isotropic shift to resemble that of CH_3OH coordinated to Ni^{2+}. However the shift for the hydroxyl protons of $Ni(CH_3OH)_6^{2+}$ is −53.1 ppm[23] while we observe a shift of only −2.49 ppm for $Ni(AcOH)_6^{2+}$. This suggests that little if any coordination of the hydroxyl group is occurring in solution.

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Registry No. $[Ni(AcOH)_6](BF_4)_2$, 20303-37-1; $Ni(H_2O)_4(AcO)_2$, 21263-98-9.

Supplementary Material Available. Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50036U-10-75.

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(1) Abbreviations used in this paper: AcO, acetate; AcOH, acetic acid.
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