

## A Three-Dimensional Study of the Crystal Structure of Nickel Acetate Tetrahydrate

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A three-dimensional X-ray analysis of nickel acetate tetrahydrate has been carried out. The crystals are monoclinic, space group  $P2_1/c$  with two molecules contained in a unit cell of dimensions  $a=4.764$ ,  $b=11.771$ ,  $c=8.425$  Å and  $\beta=93.6^\circ$ . The general structural arrangement obtained by van Niekerk & Schoening has been confirmed and new parameters obtained by Patterson and Fourier methods. The structure was refined by block-matrix least-squares calculations to a final  $R$  index of 0.068 from 800 observed reflexions collected using Cu  $K\alpha$  radiation. The hydrogen atoms were included in the calculations but their parameters were not refined. The nickel atom, located at a centre of symmetry, has a slightly distorted octahedral arrangement of oxygen atoms. Nickel–oxygen bond lengths are 2.048, 2.067 and 2.081 Å (mean e.s.d. 0.003 Å). Bond lengths and angles in the acetate ligand are in good agreement with previously reported values. The two carboxyl C–O bond lengths are 1.272 (5) and 1.255 (6) Å. Each acetate group is planar and the groups are distributed in the form of parallel sheets. The structure is extensively hydrogen-bonded. All the oxygen atoms and the water hydrogen atoms are involved. Intramolecular and intermolecular hydrogen bonds occur.

### Introduction

The crystal structures of nickel acetate tetrahydrate and the isostructural cobalt compound were first determined by van Niekerk & Schoening (1953*b*). The essential structural features which were first outlined by these authors have been confirmed in this investigation. During the course of their investigation of metal acetates van Niekerk & Schoening showed that the acetate group behaved as a bridging, monodentate and bidentate ligand.

The acetate group occurs most frequently as a bridging ligand. In addition to the examples discovered by van Niekerk & Schoening, *e.g.* chromium(II) acetate (van Niekerk & Schoening, 1953*a*) and copper(II) acetate (van Niekerk & Schoening, 1953*c*), other examples have been found in molybdenum(II) acetate (Lawton & Mason, 1965) and rhodium(II) acetate (Porai-Koshits & Antsyshkina, 1962).

These compounds have the same basic formula,  $M^{II}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , and structural arrangement. Figgis & Robertson (1965) reported bridging acetate groups in basic acetates in which the structural unit was formulated as  $[\text{M}_3(\text{CH}_3\text{COO})_6\text{O}]^+$  where  $\text{M} = \text{Fe}^{III}$  and  $\text{Cr}^{III}$ . Hessel & Romers (1969) reported bridging acetate groups in 'anhydrous manganic acetate', a linear polymer of empirical formula



in which the structural arrangement is similar to that in the basic acetates of chromium(III) and iron(III).

Bidentate acetate is much less common because of the four-membered chelate ring produced and the close approach of the carboxylate oxygen atoms. Examples have been found in zinc acetate dihydrate,



(van Niekerk, Schoening & Talbot, 1953), and sodium uranyl acetate,



(Zachariassen & Plettinger, 1959).

In bithiourea-zinc acetate (Cavalca, Gasparri, Andreotti & Domiano, 1967) the acetate group is essentially monodentate. Each acetate group has one oxygen atom which forms a short bond (1.9373, 1.954 Å) to the zinc atom, and one non-bonded oxygen atom (2.891 and 2.996 Å). The metal acetates of nickel(II) and cobalt(II) contain monodentate acetate and it is also found in some transition metal complexes, *e.g.*  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{COO})](\text{ClO}_4)_2$ , acetatopentamminecobalt(II) perchlorate.

Bidentate and monodentate acetate are much less common than the bridging acetate and accurate structural data are scarce. Consequently a three-dimensional analysis of nickel acetate tetrahydrate was undertaken in view of the presence of monodentate acetate and hydrogen bonding in the compound.

As the compound is used as a sealing agent for porous anodic oxide films on aluminum the investigation was also undertaken to provide more detailed background information on the sealing process.

### Experimental

Crystals of nickel acetate tetrahydrate, suitable for X-ray analysis, were obtained by recrystallizing the

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compound from glacial acetic acid. Long green needles elongated in the  $\{100\}$  direction were produced.

Unit-cell dimensions were calculated from photographs obtained from a Buerger precession camera using Mo  $K\alpha$  radiation ( $\lambda=0.7107 \text{ \AA}$ ) and from Weissenberg photographs using Cu  $K\alpha$  radiation.

The density was measured by flotation in a mixture of carbon tetrachloride and 1,2-dibromoethane.

#### Crystal data

$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ . F.W. 248.7

Monoclinic:

$a=4.746 \pm 0.030$ ,  $b=11.711 \pm 0.042$ ,  $c=8.425 \pm 0.031 \text{ \AA}$   
 $\beta=93.6 \pm 0.2^\circ$ .

$V=471.456 \text{ \AA}^3$ ;  $Z=2$ ;  $D_m=1.73 \text{ g.cm}^{-3}$ ;

$D_x=1.75 \text{ g.cm}^{-3}$ ;  $F(000)=260$ ;  $\mu(\text{Cu } K\alpha)=30.36 \text{ cm}^{-1}$

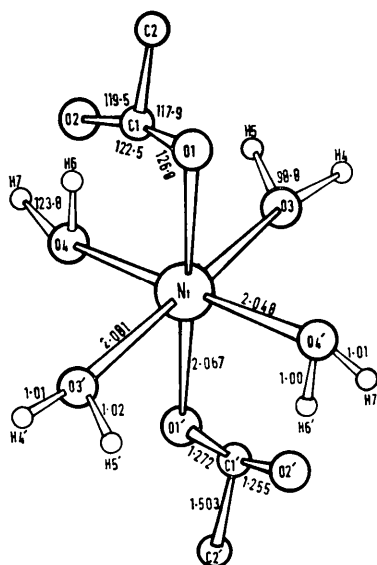


Fig. 1. Bond lengths and angles in  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ .

Space group  $P2_1/c$ , determined uniquely from systematic absences:  $h0l$  absent when  $l=2n+1$ ,  $0k0$  absent when  $k=2n+1$ .

Two small crystals of almost identical length and cross section were used for the intensity record. The first crystal had dimensions  $0.15 \times 0.21 \times 0.39 \text{ mm}$  and was used for  $a$  axis photographs ( $h=0-2$ ). The second was  $0.15 \times 0.21 \times 0.41 \text{ mm}$  and was used for  $b$  axis photographs ( $k=0-6$ ). Diffraction intensities were recorded by the equi-inclination Weissenberg, multiple-pack technique, using nickel-filtered copper radiation. Integrated intensities were measured using a Joyce-Loebl integrating microdensitometer.

Intensity data from each axis were separately processed for Lorentz and polarization corrections. The method of Monahan, Schiffer & Schiffer (1967), was used to determine interlayer scaling factors and the structure amplitudes were placed on a common scale. No correction for absorption was made. Any errors arising from extinction effects were also neglected.

#### Structure determination and refinement

The essential structural features as outlined by van Niekerk & Schoening (1953b) have been confirmed by means of three-dimensional Patterson and Fourier syntheses.

In a unit cell of nickel acetate tetrahydrate there are two molecules; consequently the two nickel atoms must lie on special positions of symmetry  $\bar{1}$ . The coordinates of all non-hydrogen atoms, determined from the Patterson synthesis were used in an initial structure-factor calculation: the  $R$  value was 0.266.

Refinement proceeded by the method of least-squares using the block-diagonal approximation. After four cycles of isotropic refinement  $R = \sum ||kF_o| - |F_c|| / \sum |kF_o|$  was 0.116. At this stage anisotropic temperature factors were generated and in a further four cycles  $R$  had fallen to 0.087. Four low-order reflexions (002, 100, 011, 112), thought to be suffering from

Table 1. Atomic parameters

The values of  $b_{ij}$  are defined by the expression  $\exp[-\frac{1}{4}(h^2a^{*2}b_{11} + 2hka^*b^*b_{12} + \dots)]$  used in the structure amplitude calculations.

	$x/a$	$y/b$	$z/c$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{13}$	$b_{12}$
Ni	0.00000	0.00000	0.00000	0.00978	0.00205	0.00568	-0.00016	-0.00415	-0.00001
O(1)	-0.23204	0.14802	0.00935	0.01276	0.00239	0.00979	-0.00167	-0.00583	0.00048
O(2)	0.07231	0.25612	0.15054	0.02308	0.00340	0.01353	-0.00430	-0.01582	0.00031
O(3)	0.27574	0.08084	-0.14509	0.01429	0.00295	0.00754	0.00132	-0.00300	0.00011
O(4)	0.23769	0.04621	0.20082	0.01673	0.00347	0.00718	-0.00094	-0.00659	-0.00086
C(1)	-0.14356	0.24466	0.25834	0.01941	0.00215	0.00759	0.00113	-0.00263	0.00104
C(2)	-0.29851	0.34843	-0.00363	0.03152	0.00310	0.01190	0.00062	-0.00392	0.00679

#### $B(\text{isotropic})$

H(1)	-0.45561	0.33450	0.06940	$3.0 \text{ \AA}^2$
H(2)	-0.24000	0.42200	0.05200	3.0
H(3)	-0.23000	0.38800	-0.09800	3.0
H(4)	0.25600	0.13700	-0.23600	3.0
H(5)	0.44000	0.11900	-0.08000	3.0
H(6)	0.17500	0.12700	0.18600	3.0
H(7)	0.43700	0.01900	0.18800	3.0



convergence had been reached. The largest indicated shift to a positional parameter, excluding hydrogen atom positions, was 0.0006 Å and to an anisotropic thermal parameter, 0.0002 Å<sup>2</sup>. In order to decide whether satisfactory weighting had been applied, batch averages of  $\sum \omega \Delta^2/n$  were calculated for ranges of  $|F_o|$  and  $\sin \theta/\lambda$ .  $\sum \omega \Delta^2/n$  was found to be reasonably independent of  $|F_o|$  and  $\sin \theta/\lambda$ .

The weighting scheme used during the final stages of refinement was:

$$\sqrt{w} = 1 / \left[ 1 + \left\{ \frac{k|F_o| - b}{a} \right\}^2 \right]^{1/2},$$

with  $a = 9.6$  and  $b = 6.0$ .

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The oxygen atom in the acetate group, O(1), complexed to the nickel(II) ion was taken as O<sup>-</sup>. The structure was also refined to an  $R$  value of 0.69 with O(1) and O(2) taken as neutral. There were no significant differences in the final parameters of either set but the data reported are those for the O<sup>-</sup> ion since this seems to be chemically more sensible. The dispersion correction (Templeton, 1962) of -3.1 electrons was added to the Ni<sup>II</sup> ion scattering factors. The imaginary part of the dispersion correction was neglected.

Atomic parameters are listed in Table 1. Table 2 contains observed and calculated structure factors.

### Description and discussion of the structure

Bond lengths and angles, together with their estimated standard deviations are listed in Table 3. Fig. 1 illustrates bond lengths and angles in the octahedron. Non-bonded distances and angles are shown in Fig. 2.

Table 3. Bond lengths and angles

	Length	e.s.d.
Ni—O(1)	2.067 Å	0.003 Å
*Ni—O(2)	3.280	0.003
Ni—O(3)	2.081	0.002

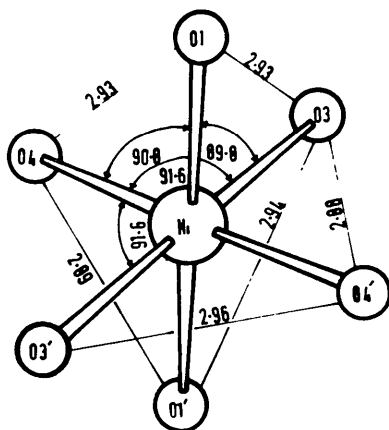


Fig. 2. Non-bonded distances and angles in the octahedron.

Table 3 (cont.)

	Length	e.s.d.
Ni—O(4)	2.048	0.003
*O(1)—O(2)	2.217	0.004
C(1)—O(1)	1.272	0.005
C(1)—O(2)	1.255	0.005
C(1)—C(2)	1.503	0.006
C(2)—H(1)	1.01	
C(2)—H(2)	1.01	
C(2)—H(3)	0.99	
O(3)—H(4)	1.01	
O(3)—H(5)	1.02	
O(4)—H(6)	1.00	
O(4)—H(7)	1.01	

	Angle	e.s.d.
O(1)—Ni—O(3)	89.8°	0.1°
O(1)—Ni—O(4)	90.8	0.1
O(3)—Ni—O(4)	91.6	0.1
O(3)—Ni—O(41)	91.6	0.1
O(1)—C(1)—O(2)	122.5	0.3
O(1)—C(1)—C(2)	117.9	0.4
O(2)—C(1)—C(2)	119.5	0.3
C(1)—O(1)—Ni	126.8	0.2
H(4)—O(3)—H(5)	99	
H(6)—O(4)—H(7)	124	
H(1)—C(2)—H(2)	93	
H(2)—C(2)—H(3)	97	
C(1)—O(2)—H(6)	103	
†O(4)—H(6)—O(2)	180	

\* Non-bonded distance.

† Intramolecular hydrogen bond.

### Configuration about the nickel atom

The nickel atom is surrounded by an octahedral arrangement of oxygen atoms. Because the nickel atom occupies a centre of symmetry at 000 the octahedron is formed from three, symmetry-related, pairs of oxygen atoms. The four oxygen atoms O(3), O(3'), O(4) and O(4') are provided by four water molecules and the remaining two oxygen atoms O(1) and O(1') are provided by two separate acetate groups. Angles within the octahedron are 90°, within experimental error, but because the Ni—O distances are significantly different from one another the octahedron must be regarded as being slightly distorted. Sacconi (1968) 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 4 contains both Ni—O(H<sub>2</sub>O) and Ni—O(carboxyl) bond lengths. The values reported by van Niekerk & Schoening (1953*b*) are significantly different from those obtained in this investigation. Although the two Ni—O(H<sub>2</sub>O) values obtained in this investigation are significantly different from each other they show good individual agreement with the data for the [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ion in NiSO<sub>3</sub>·6H<sub>2</sub>O, reported by Baggio & Becka (1969). The Ni—O(H<sub>2</sub>O) values reported by Freeman (1967), and Van der Helm & Hossain (1969), have been found in hydrated nickel(II) chelates of amino acids and imidazole derivatives. These compounds have also been a useful source of Ni—O(car-

boxyl) bond lengths. The reported values cover a wide range with that of nickel acetate tetrahydrate approximately intermediate between those reported by Van der Helm & Hossain (1969) and Freeman (1967). The averaged Ni-O bond length reported in *International Tables for X-ray Crystallography* (1962) agrees with the largest of the three reported values for this investigation.

#### Configuration of the acetate ion

The acetate ions in nickel acetate tetrahydrate are monodentate. Of the two symmetry-related acetate groups in the compound only O(1) and O(1') are bonded to the nickel atom. These two oxygen atoms, in addition to being bonded to the central carbon atom in the acetate ion, form intermolecular hydrogen bonds to O(3) and O(3') respectively in neighbouring molecules.

The remaining oxygen atoms in the two acetate groups namely O(2) and O(2') form hydrogen bonds to O(4) and to O(4') in the same molecule. This bond is intramolecular and linear. Also, they combine with O(3') and O(3) respectively in neighbouring molecules forming intermolecular hydrogen bonds. Consequently each acetate oxygen is 3-coordinate. This is the situation postulated by van Niekerk & Schoening (1953*b*) and is illustrated in Figs. 3 and 4. The two acetate groups may be regarded as planar although the deviations of atoms C(1) and C(1') from their respective mean planes may be significant. The equations of the two mean planes formed by the acetate groups are listed in Table 5. The occurrence of a centre of symmetry at each nickel atom and the existence of a twofold screw axis at  $\frac{1}{2}z$  combine to generate the acetate groups throughout the unit cell so that they form parallel sheets of atoms. The distribution of acetate ions is illustrated in Figs. 3 and 4.

Table 5. *Details of the planes of best fit*

Each plane is represented by  $lX+mY+nZ-p=0$

Plane	(1)	(2)	
(1)	$0.6284X + 0.0462Y - 0.7766Z + 0.6833 = 0$	$0.6284X + 0.0462Y - 0.7766Z - 0.6833 = 0$	
Deviations of atoms from the planes			
	Plane (1)	Plane (2)	
O(1)	0.0050 Å	O(1')	-0.0050 Å
O(2)	0.0051	O(2')	-0.0051
C(1)	-0.0141	C(1')	0.0141
C(2)	0.0041	C(2')	-0.0041

The C(2) and C(1) bond length is 1.503 Å, and agrees with 1.505 Å proposed by Brown (1959) for a

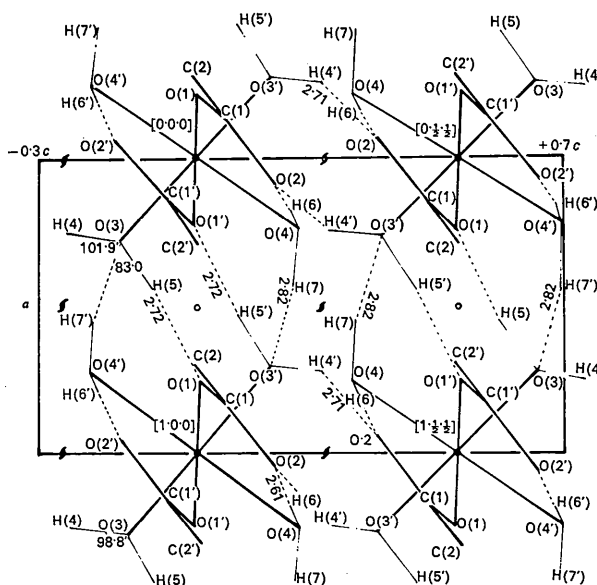
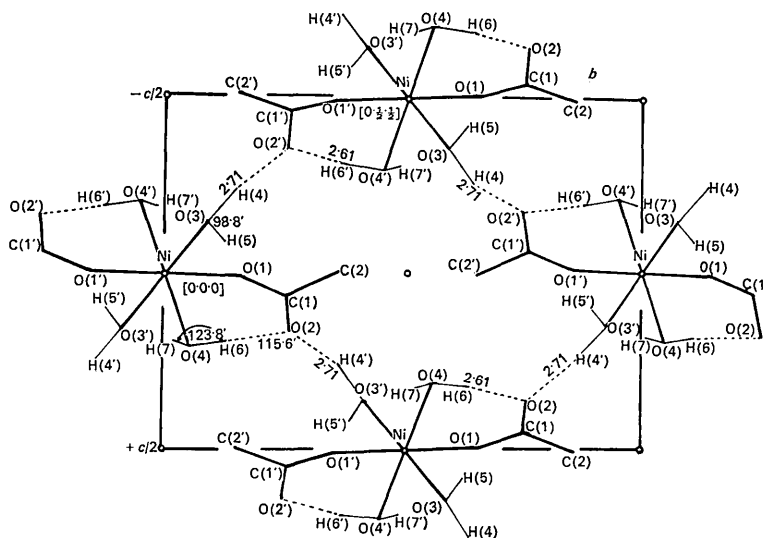


Fig. 3. [010] projection of nickel acetate tetrahydrate.

Table 4. *Comparison of nickel-oxygen bond lengths and their e.s.d.'s*

Compound	Bond length		Reference
	e.s.d.'s are in parentheses and refer to the preceding figure.		
	Ni-O(H <sub>2</sub> O)	Ni-O(carboxyl)	
Nickel acetate tetrahydrate	2.081 (2) Å 2.048 (3)	2.067 (3) Å	This investigation
Nickel acetate tetrahydrate	2.11 2.06	2.12	van Niekerk & (b) Schoening (1953)
Nickel sulphite tetrahydrate	2.043 (8) 2.076 (8)		Baggio & Becka (1969)
Averaged values obtained from amino acid and imidazole complexes of nickel(II)	2.12 (5)	2.13 (1)	Freeman (1967)
Diaquobis(L-serinato)nickel(II)	2.135 (5)	2.012 (5)	Van der Helm & Hossain (1969)
Bis(DL-histidino)nickel(II) hydrate		2.113 (8)	Fraser & Harding (1967)
averaged value of two separate determinations	-	2.08 (2)	<i>International Tables for X-ray Crystallography</i> (1962).

Fig. 4.  $a^*$  projection of nickel acetate tetrahydrate.

$\sigma$ -bond formed between  $sp^3$  and  $sp^2$  hybridized carbon atoms. Van Niekerk & Schoening (1953*b*) reported 1.56 Å.

The C(1)–O(1) and C(1)–O(2) bond lengths of the carboxyl group are 1.272(5) and 1.255(5) Å. The difference is probably significant; van Niekerk & Schoening (1953*b*) reported corresponding lengths of 1.31 and 1.29 Å. The values are significantly lower in this investigation. The separation distance between the two carboxylate oxygen atoms is 2.217(4) Å in this investigation and 2.27 Å in that of van Niekerk & Schoening (1953*b*). Very close agreement has been observed between the bond lengths and angles of the carboxylate groups in diaquobis-(L-serinato)nickel(II) (Van der Helm & Hossain, 1969) and those in this investigation. Fig. 5 illustrates the respective values.

Hahn (1957) has proposed that in a fully ionized carboxyl group the C–O bond lengths should make equal angles of  $115.7^\circ$  with the C–C bond. The corresponding angles in this investigation are O(1)–C(1)–C(2) =  $117.9^\circ$  and O(2)–C(1)–C(2) =  $119.5^\circ$ . The latter angle, involving the intramolecular hydrogen-bonded O(2) atom, is significantly different from Hahn's value. The O(2)–C(1)–O(2) bond angle, proposed by Hahn

to be  $126^\circ$ , is  $122.5^\circ$  in this investigation; van Niekerk & Schoening (1953*b*) reported  $121^\circ 39'$ .

It would seem that the acetate groups in nickel acetate tetrahydrate are fully ionized and that differences in bond-order between the two C–O bonds are minimal. Deviations from a regular, fully ionized carboxyl group should be attributed to the requirements of hydrogen bonding.

### Hydrogen bonding

The compound is extensively hydrogen bonded. All oxygen atoms and water hydrogen atoms are involved. The small anisotropic temperature vibrations ( $b_{12}$  and  $b_{23}$ , Table 1) in the  $ab$  and  $bc$  planes are indicative of extensive hydrogen bonding in these directions. Fig. 4 illustrates the acetate oxygen atom involvement in the hydrogen bonding scheme and Fig. 3 shows the arrangement of the intermolecular hydrogen bonding in the [010] projection. Individual bond lengths and angles are listed in Table 6.

Table 6. *Hydrogen-bond distances and angles*

Equivalent position			Symmetry code	
$x$	$y$	$z$		1
$-x$	$-y$	$-z$		2
$-x$	$\frac{1}{2} + y$	$\frac{1}{2} - z$		3
$x$	$\frac{1}{2} - y$	$\frac{1}{2} + z$		4
Atom A	Atom B	Symmetry code	Cell	Length (A–B)
*O(4)	O(2)	1	0, 0, 0	2.619 Å
*O(4')	O(2')	1	0, 0, 0	2.619
O(2)	O(3')	3	0, 0, 0	2.716
O(1)	O(3)	1	-1, 0, 0	2.725
O(1')	O(3')	1	1, 0, 0	2.725
O(3)	O(4')	1	1, 0, 0	2.820
O(3')	O(4)	1	-1, 0, 0	2.820
O(2')	O(3)	3	0, -1, -1	2.716

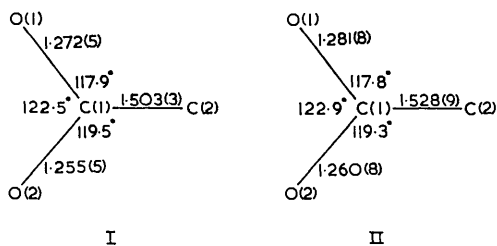


Fig. 5. Bond lengths and angles in the carboxylate groups of I, nickel acetate tetrahydrate and II, diaquobis-(L-serinato)-nickel(II).

Table 6 (cont.)

Hydrogen bond	Angle
*O(2)–H(6)–O(4)	180°
*O(2)–H(6')–O(4')	180
O(2)–H(4')–O(3')	154
O(2')–H(4)–O(3)	154
O(1)–H(5)–O(3)	165
O(1')–H(5')–O(3')	165
O(3)–H(7')–O(4')	155
O(3')–H(7)–O(4)	155

\* Intramolecular hydrogen bond.

The original hydrogen bonding scheme, proposed by van Niekerk & Schoening (1953*b*) was based on non-bonded contacts between neighbouring oxygen atoms. The essential features of their scheme have been confirmed in this investigation but location of the water hydrogen atoms indicated additional intermolecular hydrogen bonds between neighbouring water molecules.

A convenient description of the hydrogen-bonded network can be made by reference to the two pairs of water molecules coordinated to the nickel atom. These molecules are H(4)–O(3)–H(5), H(6)–O(4)–H(7) and their symmetry-related partners H(4')–O(3')–H(5') and H(6')–O(4')–H(7').

The water oxygen atoms O(3) and O(3') are four coordinate and possess a distorted tetrahedral configuration of one nickel–oxygen bond and three hydrogen bonds. The hydrogen bonds are intermolecular. In two instances acetate oxygen atoms O(1), O(1'), and O(2), O(2') are involved; in the third case it is the water oxygen atoms O(4), O(4') which are involved. All the bonds exhibit distortion from linearity. In addition, O(3) and O(3') behave as acceptor atoms to the acetate oxygen atoms and as donor atoms to the O(4), O(4') water oxygen atoms.

In the molecules H(6)–O(4)–H(7) and H(6')–O(4')–H(7') the oxygen atoms are three coordinate and adopt a distorted trigonal planar configuration consisting of one nickel oxygen bond, one intramolecular, linear hydrogen bond O(4)–H(6)···O(2) and one intermolecular hydrogen bond O(4)–H(7)···O(3') in which significant distortion from linearity occurs.

In these bonds and those formed by the symmetry-related O(4') atom both oxygen atoms behave as acceptor atoms.

Hydrogen bonding is of considerable importance in this structure and probably accounts for the differences in the octahedral nickel–oxygen bond-lengths and for the observed variations in the parameters of the acetate ion.

### Computing

All calculations were performed on an IBM 1620 computer in the Department of Mathematics, Statis-

tics and Computing, the Polytechnic, Newcastle upon Tyne.

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