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Key indicators

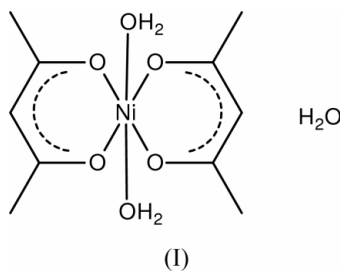
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
H-atom completeness 91%
R factor = 0.040
wR factor = 0.111
Data-to-parameter ratio = 14.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Electrochemical synthesis and a redetermination of
 $\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$

The title complex, bis(acetylacetonato)diaquanickel(II) monohydrate, $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, was easily synthesized in high yield by electrochemical dissolution of nickel metal in an acetylacetonone and ethanol solution *via* direct hydrolysis of the electrolyte solution at a temperature of 333 K. The crystal structure shows octahedral coordination of nickel with two *trans* aqua ligands. An uncoordinated water molecule engages in hydrogen bonding.

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Comment

The paramagnetic complex $\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2$ (acac = acetylacetonato) has been a subject of interest to chemists for the past two decades (Abernathy & Sharp, 1997; Sharp *et al.*, 1997; Miller *et al.*, 2000; Lohr *et al.*, 1999), following the earlier report of trinuclear molecules in the crystal structure of $\text{Ni}(\text{acac})_2$ (Bullen, 1956). Paramagnetic transition metal ions in solution can produce large nuclear magnetic resonance (NMR) relaxation enhancements of nuclear spins in ligand species and in solvent molecules. This phenomenon, called NMR paramagnetic relaxation enhancement or NMR-PRE, has been used widely to probe the structure, dynamics and magnetic properties of dissolved paramagnetic species. Crystal structures of suitable paramagnetic complexes provide structural data to aid NMR-PRE study (Sharp *et al.*, 1997).



Recently, electrochemical dissolution of a nickel anode in acetylacetonone and ethanol solution was carried out in our laboratory (Zhou *et al.*, 2000*a,b*, 2001). Some water was added to the electrolyte to produce hydrolysis and prepare nanometer NiO by a sol-gel process at room temperature. The complex $\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2$ crystallized out of the solution.

The molecular structure is essentially the same as that reported by Montgomery & Lingafelter (1964) for this complex without water of crystallization. Though Misra *et al.* (1979) considered it was not possible to produce a single crystal of $\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2$, it was very easy for us to obtain one by using an electrochemical method. Because of our interest in sol-gel chemistry, the electrolyte solution with some

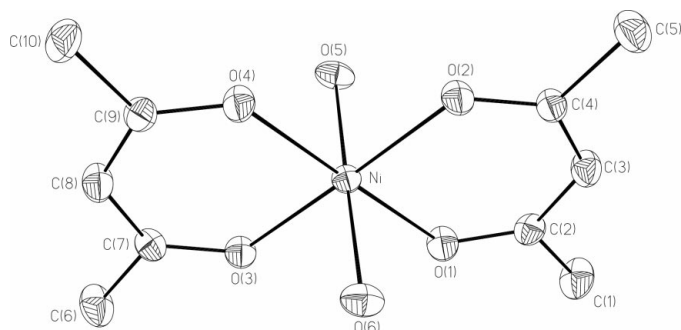


Figure 1
The molecular structure of (I) with ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

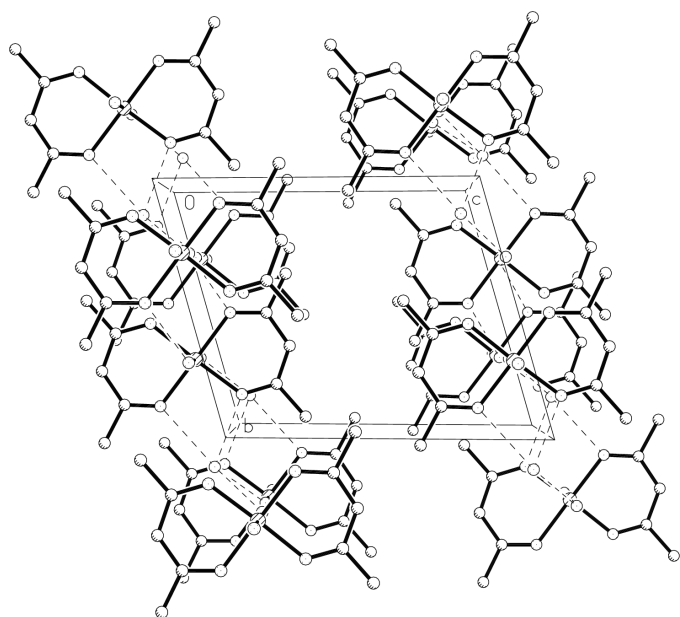


Figure 2
The packing viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

added water was heated to 333 K for 30 min. Crystals of hydrated $\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$, (I), were also obtained and the crystal structure has been determined. Each of the two products can be obtained preferentially by controlling the hydrolysis temperature carefully. Harlow & Pfluger (1973) obtained crystals of the hydrate by using a completely different method previously. The structure reported here is of greater precision.

Selected bond lengths and angles are given in Table 1, and the molecular structure is shown in Fig. 1, with a packing diagram shown in Fig. 2. The uncoordinated water molecule is involved in hydrogen bonding, and further hydrogen bonding links coordinated water molecules to acac ligands in adjacent molecules (Table 2).

In the structure without water of crystallization, the nickel ion has acac O atoms at 2.021 and 2.014 Å and water O atoms at 2.139 Å in a precisely centrosymmetric arrangement. In the

hydrated structure, the corresponding distances are 1.994 (2)–2.031 (2) Å for acac, and 2.075 (2) and 2.080 (2) Å for water ligands, respectively, the nickel ion lying in a general position but retaining an octahedral coordination.

Experimental

Metallic nickel was electrochemically dissolved in the presence of tetrabutylammonium bromide as supporting electrolyte. Pure nickel foil (AR 99.99%, $2 \times 4 \times 0.05$ cm) was used as cathode and anode. The electrochemical reaction was carried out in a cell without separating the cathode and anode space. 250 ml (2.5 mol) ethanol was poured into the electrolysis bath, as solvent and as reagent. During the electrolysis process, 5 ml (0.05 mol) acetylacetonone was gradually added dropwise to the electrolyte. The potential across the anode was adjusted so that a current of 0.2 A passed through the cell for 6 h. Crystals of the title compound were produced.

Crystal data

$[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$
 $M_r = 310.97$
 Triclinic, $P\bar{1}$
 $a = 7.5572$ (15) Å
 $b = 9.0637$ (18) Å
 $c = 10.997$ (2) Å
 $\alpha = 74.17$ (3)°
 $\beta = 84.50$ (3)°
 $\gamma = 89.74$ (3)°
 $V = 721.2$ (2) Å³

$Z = 2$
 $D_x = 1.432$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 20 reflections
 $\theta = 15.4$ – 22.9 °
 $\mu = 1.37$ mm⁻¹
 $T = 293$ (2) K
 Plate, blue–green
 $0.50 \times 0.40 \times 0.30$ mm

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.462$, $T_{\max} = 0.664$
 3104 measured reflections
 2659 independent reflections
 2459 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 26.0$ °
 $h = -9 \rightarrow 9$
 $k = -11 \rightarrow 0$
 $l = -13 \rightarrow 13$
 3 standard reflections
 every 300 reflections
 intensity decay: 1.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.111$
 $S = 1.04$
 2659 reflections
 179 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2 + 0.2124P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.67$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.46$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni—O2	1.9958 (19)	Ni—O4	2.030 (2)
Ni—O3	2.008 (2)	Ni—O6	2.073 (2)
Ni—O1	2.025 (2)	Ni—O5	2.076 (2)
O2—Ni—O3	177.73 (7)	O1—Ni—O6	89.64 (10)
O2—Ni—O1	91.65 (8)	O4—Ni—O6	91.09 (10)
O3—Ni—O1	90.55 (8)	O2—Ni—O5	90.20 (9)
O2—Ni—O4	87.82 (8)	O3—Ni—O5	90.42 (9)
O3—Ni—O4	89.99 (8)	O1—Ni—O5	88.52 (10)
O1—Ni—O4	179.09 (8)	O4—Ni—O5	90.75 (10)
O2—Ni—O6	89.69 (9)	O6—Ni—O5	178.15 (9)
O3—Ni—O6	89.76 (9)		

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O6–H4 \cdots O7 ⁱ	0.819 (19)	2.20 (5)	2.799 (3)	130 (5)
O5–H1 \cdots O7 ⁱⁱ	0.816 (18)	2.08 (3)	2.781 (3)	144 (4)
O6–H3 \cdots O4 ⁱⁱⁱ	0.804 (19)	2.13 (2)	2.903 (3)	161 (5)
O5–H2 \cdots O2 ^{iv}	0.81 (2)	2.65 (5)	3.237 (3)	131 (6)
O5–H2 \cdots O4 ^{iv}	0.81 (2)	2.22 (4)	2.929 (3)	147 (6)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$; (iii) $-x, 1-y, -z$; (iv) $1-x, 1-y, -z$.

H atoms bonded to carbon were constrained with a riding model. H atoms of the coordinated water molecules were refined with isotropic displacement parameters, and with restraints on O–H bond lengths, but no H atoms were included for the uncoordinated water.

Data collection: *AFC-5R Diffractometer Control Software* (Rigaku, 1988); cell refinement: *AFC-5R Diffractometer Control Software*; data reduction: *MoIEN/VAX* in *CAD-4 Operations Manual* (Enraf–Nonius, 1977); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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