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Key indicators

Single-crystal X-ray study
 T = 100 K
 Mean $\sigma(C-C)$ = 0.003 Å
 R factor = 0.031
 wR factor = 0.087
 Data-to-parameter ratio = 18.8

For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

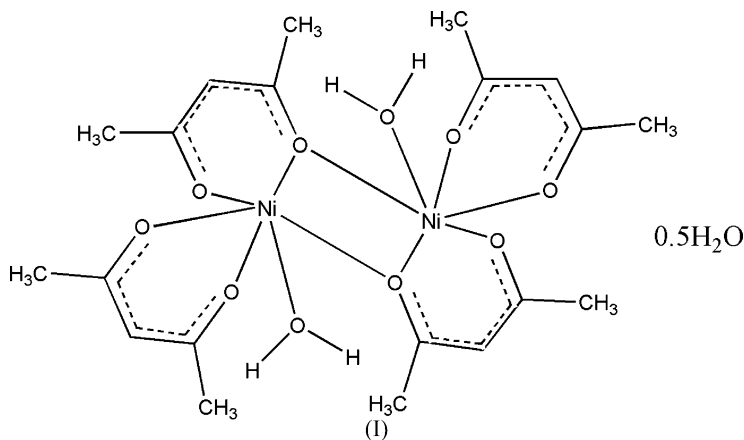
**Bis(μ -acetylacetonato- $\kappa^2O:O'$)bis[(acetyl-
 acetonato- κ^2O,O')aquanickel(II)] hemihydrate**

The structure of the title complex, $[Ni_2(C_5H_7O_2)_4(H_2O)_2] \cdot 0.5H_2O$, is dimeric and corresponds to the trimeric structure of bis(acetylacetonato)nickel(II) in which one $Ni(acac)_2$ unit is replaced by two water molecules. The centrosymmetric molecule comprises two O–O edge-shared octahedra. The asymmetric unit contains two half-molecules of the complex and one water molecule.

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Comment

The solid-state structure for octahedral complexes of the type $[M(acac)_2(L)]_2$ ($M = Ni, Co$; $acac =$ acetylacetonate; $L =$ alcohols, amines) have recently been reported (Kessler *et al.*, 2003; O'Connor *et al.*, 1984; He, Yao, Luo, Zhang & Wu, 2003; He, Yao, Luo, Zhang, Lui, Zhang & Wu, 2003; Doring *et al.* 1997). Such complexes are potential precursors for chemical vapor deposition to form ceramic oxides, for example NiO, which is used in ceramic material applications. Such types of metal β -diketonates are also important for the synthesis of heterobimetallic complexes, which are of interest as precursors for mixed metal oxide materials.



The asymmetric unit contains two half-molecules of the complex and one water molecule. The complex molecules are centrosymmetric. The two molecules with identical cell parameters as in (I) are connected to each other by hydrogen bonds between the coordinated and the uncoordinated water molecules through hydrogen bonds (Table 2)

The centrosymmetric dimeric monohydrate, $[Ni(acac)_2 \cdot H_2O]_2$, corresponds to trimeric $[Ni(acac)_2]_3$ (Bullen *et al.*, 1965; Hursthouse *et al.*, 1982), with two positions that were filled by bridges from the terminal $Ni(acac)_2$ units being occupied by the O atoms of water molecules. The structural parameters found here are only slightly different from those

determined for $[\text{Ni}(\text{acac})_2]_3$ and from that of the cobalt analog $[\text{Co}(\text{acac})_2\text{H}_2\text{O}]_2$ of the title compound (Cotton & Elder, 1966). The bridging acac rings in this structure are approximately coplanar with the chelate rings. The Ni—O_{acac} bridging bonds are slightly longer than the Ni—O_{acac} non-bridging bonds, and the average Ni—O bond lengths is 2.073 Å, which is in good agreement with the 2.069 and 2.065 Å found in $[\text{Ni}(\text{acac})_2]_3$ and $[\text{Ni}_2(\text{acac})_4(\text{py})]$, respectively (Hursthouse *et al.*, 1982). The average Ni···Ni distance in (I) is 3.16 Å, which is similar to the values found for other dimeric complexes of this kind, but significantly larger than that found in the trimer (2.89 Å), which is because the steric strain has reduced the average ‘bite’ angle of the acac ligands of only 85.10, compared with 99.8° observed for compound (I). The average O—Ni—O ‘bite’ angles of the acac ligand in (I), on the other hand, are very close to 90° (91.77° for the O_{water}—Ni—O_{acac} angles and 90.91° for the others), indicating an only very slight distortion of the octahedral environment around the central Ni^{II} ion.

Experimental

$[\text{Ni}(\text{acac})_2] \cdot 2\text{H}_2\text{O}$ (0.5 g, 1.9 mmol) was dissolved in toluene (5 ml) in a two-necked flask fitted with a reflux condenser, magnetic stirrer and a vacuum line attachment. The contents were heated to 353 K for 10 min and the resulting solution was filtered to remove the traces of undissolved $[\text{Ni}(\text{acac})_2] \cdot 2\text{H}_2\text{O}$. Green crystals with a melting point of 448 K suitable for single-crystal X-ray analysis were grown in 90% yield by slow evaporation of the toluene solution at room temperature. The crystals were difficult to cut without shattering and thus one crystal with the dimensions 0.50 × 0.42 × 0.33 mm was used without an attempt to cut it below the approximate size of the X-ray beam of 0.5 mm.

Crystal data

$[\text{Ni}_2(\text{C}_5\text{H}_7\text{O}_2)_4(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$	$Z = 4$
$M_r = 567.89$	$D_x = 1.488 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 14.6463 (6) \text{ \AA}$	$\mu = 1.55 \text{ mm}^{-1}$
$b = 17.1089 (7) \text{ \AA}$	$T = 100 (2) \text{ K}$
$c = 10.1294 (4) \text{ \AA}$	Block, green
$\beta = 98.042 (1)^\circ$	$0.50 \times 0.42 \times 0.33 \text{ mm}$
$V = 2513.28 (18) \text{ \AA}^3$	

Data collection

Bruker SMART APEX CCD diffractometer	12866 measured reflections
ω scans	6087 independent reflections
Absorption correction: multi-scan (SADABS in SAINT-Plus; Bruker, 2003)	5432 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.510$, $T_{\max} = 0.600$	$R_{\text{int}} = 0.016$
	$\theta_{\text{max}} = 28.3^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 1.731P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.087$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$
6087 reflections	$\Delta\rho_{\text{min}} = -0.71 \text{ e \AA}^{-3}$
324 parameters	
H atoms treated by a mixture of independent and constrained refinement	

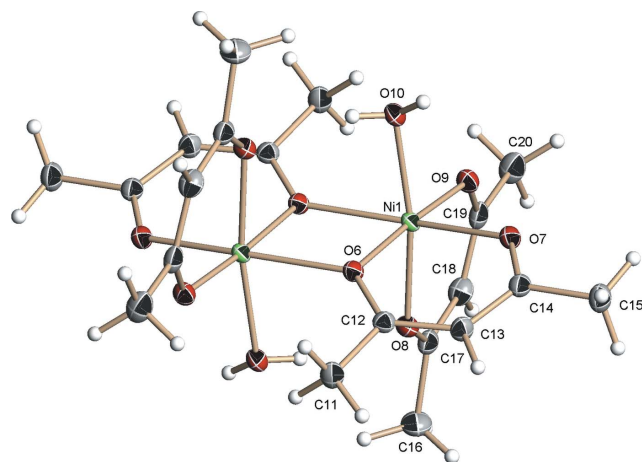


Figure 1

View of one of the two independent complex molecules of (I), with 50% probability displacement ellipsoids. Unlabeled atoms are related to labeled atoms by $(-x, -y, -z)$. The solvent water molecule is not shown. The second molecule is essentially the same.

Table 1

Selected geometric parameters (Å, °).

Ni1—O9	1.9921 (13)	Ni2—O1	1.9897 (13)
Ni1—O8	2.0221 (13)	Ni2—O2	2.0151 (13)
Ni1—O7	2.0265 (12)	Ni2—O4	2.0242 (13)
Ni1—O6	2.0487 (12)	Ni2—O3	2.0333 (13)
Ni1—O10	2.0835 (13)	Ni2—O5	2.0921 (14)
Ni1—O6 ⁱ	2.1139 (12)	Ni2—O3 ⁱⁱ	2.1138 (12)
O9—Ni1—O8	91.12 (5)	O1—Ni2—O2	91.83 (6)
O9—Ni1—O7	89.65 (5)	O1—Ni2—O4	85.39 (5)
O8—Ni1—O7	95.84 (5)	O2—Ni2—O4	95.85 (5)
O9—Ni1—O6	175.99 (5)	O1—Ni2—O3	176.06 (5)
O8—Ni1—O6	84.94 (5)	O2—Ni2—O3	88.99 (5)
O7—Ni1—O6	90.05 (5)	O4—Ni2—O3	90.69 (5)
O9—Ni1—O10	93.35 (5)	O1—Ni2—O5	91.03 (6)
O8—Ni1—O10	170.62 (5)	O2—Ni2—O5	169.58 (6)
O7—Ni1—O10	92.44 (5)	O4—Ni2—O5	94.36 (5)
O6—Ni1—O10	90.66 (5)	O3—Ni2—O5	88.84 (5)
O6—Ni1—O6 ⁱ	81.21 (5)	O3—Ni2—O3 ⁱⁱ	79.25 (5)
O10—Ni1—O6 ⁱ	82.47 (5)	O5—Ni2—O3 ⁱⁱ	82.03 (5)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H5D···O7	0.813 (17)	1.984 (17)	2.7887 (18)	170 (3)
O5—H5E···O2 ⁱⁱ	0.831 (17)	2.106 (18)	2.906 (2)	161 (2)
O10—H10E···O8 ⁱ	0.816 (16)	2.051 (17)	2.8494 (18)	166 (2)
O10—H10D···O4	0.843 (16)	1.924 (17)	2.7649 (19)	175 (3)
O11—H11D···O9	0.970 (18)	1.96 (2)	2.890 (2)	160 (3)
O11—H11E···O1	0.972 (18)	1.870 (19)	2.836 (2)	173 (3)

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

Water H atoms were located in a difference density Fourier map. O—H distances for the two coordinated and the uncoordinated water molecules were each set to be the same within a standard deviation of 0.02. All other H atoms were placed geometrically and treated as riding. All H atoms were refined with an isotropic displacement parameter 1.5 (methyl, water) or 1.2 (all others) times U_{eq} of the neighboring C or O atom. Methyl H atoms were allowed to rotate to best fit the experimental electron density.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE-Plus* (Bruker, 2003); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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