Bis(3-acetyl-6-methyl-2-oxo-2H-pyran-4-olato)bis(dimethyl sulfoxide)nickel(II)

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In the title compound, $[\text{Ni}(\text{C}_8\text{H}_7\text{O}_4)_2\{(\text{CH}_3)_2\text{SO}\}_2]$, the Ni^{II} atom is located on a crystallographic centre of symmetry and has a distorted octahedral coordination geometry of type $M\text{O}_6$. The bidentate dehydroacetic acid (DHA) ligands occupy the equatorial plane of the complex in a *trans* configuration, and the dimethyl sulfoxide (DMSO) ligands are weakly coordinated through their O atoms in the axial positions.

Related literature

3-Acetyl-4-hydroxy-6-methyl-2-oxo-2H-pyran (dehydroacetic acid) (Arndt *et al.*, 1936) is a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems (Tan & Ang, 1988). It has been shown to possess modest antifungal properties, see: Rao *et al.* (1978). For natural fungicides possessing structures analogous to 5,6-dihydrodehydroacetic acid, see: Bartels-Keith (1960); Miyakado *et al.* (1982); Ayer *et al.* (1988). The complexes of DHA with copper and with several other transition metal cations are fungistatic, see: Rao *et al.* (1978). For the nickel–DHA complex, see: Casabò *et al.* (1987). The configuration of the complex molecule is similar to that found in [Zn(DHA)₂·2(DMSO) and Cd(DHA)₂·2(DMSO)] (Zucolotto Chalaça *et al.*, 2002), [Cu(DHA)₂·2(DMSO)] (Djedouani *et al.*, 2006) and bis(4,6-dibromo-2-formylphenolato-$\kappa^2 O,O'$)-bis(dimethyl sulfoxide)nickel(II) (Zhang *et al.*, 2007). For Ni—O$_{\text{DMSO}}$ distances in similar structures, see: Ma *et al.* (2003); Tahir *et al.* (2007); Zhang *et al.* (2007).
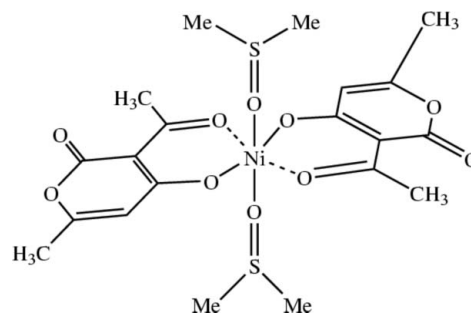
Experimental

Crystal data

$[\text{Ni}(\text{C}_8\text{H}_7\text{O}_4)_2(\text{C}_2\text{H}_6\text{OS})_2]$	$V = 1177.40\ (16)$ Å^3
$M_r = 549.24$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.3850\ (10)$ Å	$\mu = 1.05$ mm^{-1}
$b = 6.2833\ (4)$ Å	$T = 100$ K
$c = 19.7434\ (15)$ Å	$0.25 \times 0.15 \times 0.10$ mm
$\beta = 123.525\ (6)°$	

Data collection

Nonius KappaCCD diffractometer	14084 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2628 independent reflections
	1962 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.902$, $T_{\max} = 0.902$	$R_{\text{int}} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	156 parameters
$wR(F^2) = 0.098$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\max} = 0.55$ e Å^{-3}
2628 reflections	$\Delta\rho_{\min} = -0.97$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—O2	1.9849 (16)	Ni1—O1	2.1255 (18)
Ni1—O3	2.0159 (15)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$B$$\cdots$O4$^{\text{ii}}$	0.96	2.55	3.384 (4)	145
C2—H2$B$$\cdots$O4$^{\text{ii}}$	0.96	2.53	3.370 (4)	146
C2—H2$C$$\cdots$O2$^{\text{iii}}$	0.96	2.46	3.378 (4)	160

Symmetry codes: (ii) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x, y + 1, z$.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

metal-organic compounds

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2559).

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supplementary materials

Bis(3-acetyl-6-methyl-2-oxo-2*H*-pyran-4-olato)bis(dimethyl sulfoxide)nickel(II)

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Comment

3-Acetyl-4-hydroxy-6-methyl-2-oxo-2*H*-pyran (dehydroacetic acid) (Arndt *et al.*, 1936) is a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems (Tan & Ang, 1988). It has been shown to possess modest antifungal properties (Rao *et al.*, 1978). The importance of similar pyrones as potential fungicides is reinforced by the existence of several natural fungicides possessing structures analogous to 5,6-dihydrodehydroacetic acid, such as alternaric acid (Bartels-Keith, 1960), the podoblastins (Miyakado *et al.*, 1982) and lachnelluloic acid (Ayer *et al.*, 1988). Also, it has been shown that the complexes of DHA with copper and with several other transition metal cations are fungistatic (Rao *et al.*, 1978). This has motivated our study of the structural characterization of complexes of dehydroacetic acid. The complex of DHA with nickel was previously reported by Casabò *et al.* (1987), but their characterization of the compound was based only on thermal and elemental analysis, and on IR and NMR spectroscopy.

We present here the crystal structure determination of the title complex, [Ni(DHA)$_2$.2(DMSO)], (I) (DMSO = dimethyl-sulfoxide). The nature of the title compound, (I), was established by an X-ray structure determination and is shown in Fig. 1

The Ni atom lies on a crystallographic centre of symmetry with the ligands bonded to nickel in an all-*trans* fashion. The configuration of the complex molecule is similar to that found in [Zn(DHA)$_2$. 2(DMSO); Cd(DHA)2.2(DMSO)] (Zucolotto Chalaça *et al.*, 2002), [Cu(DHA)$_2$. 2(DMSO)] (Djedouani *et al.*, 2006), with (DHA: dehydroacetic acid) and Bis(4,6-dibromo-2-formylphenolato-κ^2 *O,O'*)-bis(dimethyl sulfoxide)nickel(II), [Ni(C$_7$H$_3$Br$_2$O$_2$)$_2$(C$_2$H$_6$OS)$_2$] (Zhang *et al.*, 2007).

The coordination polyhedron around the Ni atom is a slightly distorted octahedron (Table 1), with the O atoms of the DMSO groups in axial positions; and the Ni—O$_{DMSO}$ distance is in agreement with literature values: [2.1139 (12) Å - 1.9897 (13) Å (Tahir *et al.*, 2007), 1.998 (3) Å - 2.105 (3) Å (Zhang *et al.* 2007), 2.030 (2) Å- 2.057 (2)Å (Ma *et al.*, 2003)].

The orientation of the DMSO molecule can be described by the torsion angles O3—Ni—O1—S [43.32 (4) °] and O2—Ni—O1—S [-137.70 (4) °]. The packing of (I) is stabilized by weak intermolecular C—H···O hydrogen bonds (Table 2) which form a three-dimensional network (Fig. 2).

Experimental

Compound (I) was prepared by the reaction of dehydroacetic acid with nickel (II) chloride hexahydrate in the presence of sodium acetate (Casabò *et al.* 1987). Crystals of (I) were grown by slow evaporation of a dimethylsulfoxide solution..

Refinement

H atoms were positioned geometrically and treated as riding, with C—H = 0.93 Å with U_{iso}(H) = 1.2Ueq(C). The methyl H atoms were constrained to an ideal geometry (C—H = 0.96 Å) with U_{iso}(H) = 1.2U_{eq}(C), but were allowed to rotate freely about the C—C bonds.
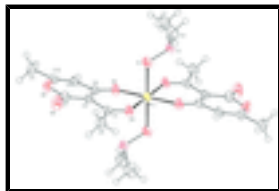
supplementary materials

Figures

Fig. 1. The independent components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
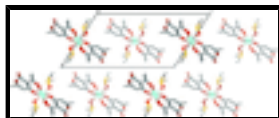

Fig. 2. The crystal packing of (I); Hydrogen atoms have been omitted for clarity.

Bis(3-acetyl-6-methyl-2-oxo-2*H*-pyran-4-olato)bis(dimethyl sulfoxide)nickel(II)

Crystal data

$[Ni(C_8H_7O_4)_2(C_2H_6OS)_2]$	$F_{000} = 572$
$M_r = 549.24$	$D_x = 1.549$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2190 reflections
$a = 11.3850 (10)$ Å	$\theta = 2.8–27.3°$
$b = 6.2833 (4)$ Å	$\mu = 1.05$ mm^{-1}
$c = 19.7434 (15)$ Å	$T = 100$ K
$\beta = 123.525 (6)°$	Plates, colourless
$V = 1177.40 (16)$ Å^3	$0.25 \times 0.15 \times 0.1$ mm
$Z = 2$	

Data collection

Nonius KappaCCD diffractometer	2628 independent reflections
Radiation source: fine-focus sealed X-ray tube	1962 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.071$
$T = 100$ K	$\theta_{max} = 27.5°$
φ scans, and ω scans with κ offsets	$\theta_{min} = 3.5°$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$h = -14 \rightarrow 14$
$T_{min} = 0.902$, $T_{max} = 0.902$	$k = -8 \rightarrow 7$
14084 measured reflections	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2 + 0.3428P]$ where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.098$	$(\Delta/\sigma)_{max} = 0.001$	
$S = 1.11$	$\Delta\rho_{max} = 0.55$ e Å^{-3}	
2628 reflections	$\Delta\rho_{min} = -0.97$ e Å^{-3}	
156 parameters	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$	
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0084 (19)	
Secondary atom site location: difference Fourier map		

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Ni1	0.5	0.5	0.5	0.02521 (16)
S1	0.75777 (6)	0.76611 (10)	0.53190 (4)	0.03283 (19)
O5	0.22643 (18)	0.1935 (3)	0.18093 (9)	0.0384 (4)
O1	0.62169 (17)	0.6626 (3)	0.46467 (10)	0.0387 (4)
O2	0.47029 (16)	0.2626 (3)	0.42577 (9)	0.0307 (4)
O3	0.32165 (16)	0.6292 (3)	0.40600 (9)	0.0316 (4)
O4	0.1020 (2)	0.4798 (3)	0.15900 (11)	0.0478 (5)
C6	0.2779 (2)	0.4022 (4)	0.29848 (13)	0.0252 (5)
C3	0.1192 (3)	0.7190 (4)	0.28219 (15)	0.0378 (6)
H3A	0.1101	0.8133	0.3173	0.057*
H3B	0.0368	0.631	0.2527	0.057*
H3C	0.1291	0.801	0.2446	0.057*
C10	0.3256 (3)	0.0457 (4)	0.23083 (15)	0.0317 (6)
C8	0.3859 (2)	0.2500 (4)	0.34964 (14)	0.0253 (5)
C9	0.3994 (2)	0.0651 (4)	0.31075 (14)	0.0296 (5)
H9	0.4616	−0.0426	0.3428	0.036*
C5	0.2474 (2)	0.5807 (4)	0.33237 (13)	0.0265 (5)
C2	0.7743 (3)	1.0036 (4)	0.48915 (18)	0.0469 (7)
H2A	0.7626	0.9718	0.4382	0.07*
H2B	0.8659	1.0642	0.5256	0.07*
H2C	0.7034	1.1033	0.4805	0.07*
C7	0.1958 (2)	0.3697 (4)	0.21184 (14)	0.0312 (6)
C4	0.3357 (3)	−0.1273 (5)	0.18287 (17)	0.0470 (7)
H4A	0.4053	−0.2289	0.2191	0.071*
H4B	0.3623	−0.0679	0.1484	0.071*
H4C	0.246	−0.1966	0.1501	0.071*
C1	0.8954 (3)	0.6199 (5)	0.53594 (19)	0.0526 (8)
H1A	0.8972	0.4776	0.5542	0.079*
H1B	0.9841	0.6879	0.573	0.079*

H1C	0.8792	0.6154	0.4828	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0190 (2)	0.0297 (3)	0.0197 (2)	0.00047 (17)	0.00610 (17)	−0.00322 (16)
S1	0.0280 (3)	0.0421 (4)	0.0247 (3)	−0.0061 (3)	0.0122 (3)	−0.0037 (3)
O5	0.0403 (10)	0.0450 (11)	0.0241 (9)	0.0070 (8)	0.0141 (8)	−0.0024 (7)
O1	0.0292 (9)	0.0534 (11)	0.0275 (9)	−0.0120 (8)	0.0119 (8)	−0.0051 (8)
O2	0.0245 (8)	0.0336 (9)	0.0212 (8)	0.0057 (7)	0.0046 (7)	−0.0021 (7)
O3	0.0257 (8)	0.0336 (10)	0.0260 (9)	0.0043 (7)	0.0083 (7)	−0.0040 (7)
O4	0.0461 (12)	0.0539 (12)	0.0237 (9)	0.0148 (10)	0.0068 (8)	0.0052 (8)
C6	0.0210 (11)	0.0284 (13)	0.0226 (11)	−0.0001 (10)	0.0099 (9)	0.0003 (9)
C3	0.0292 (13)	0.0375 (15)	0.0335 (13)	0.0092 (11)	0.0090 (11)	−0.0011 (11)
C10	0.0273 (13)	0.0352 (14)	0.0342 (13)	−0.0012 (11)	0.0179 (11)	−0.0038 (10)
C8	0.0209 (11)	0.0285 (12)	0.0255 (11)	−0.0034 (10)	0.0122 (9)	−0.0008 (9)
C9	0.0225 (12)	0.0309 (13)	0.0286 (13)	0.0003 (10)	0.0098 (10)	−0.0023 (10)
C5	0.0202 (11)	0.0286 (13)	0.0266 (12)	−0.0018 (10)	0.0104 (10)	0.0025 (9)
C2	0.0358 (15)	0.0372 (16)	0.0524 (17)	0.0002 (12)	0.0148 (13)	0.0047 (12)
C7	0.0292 (13)	0.0347 (14)	0.0264 (12)	0.0010 (11)	0.0132 (10)	0.0013 (10)
C4	0.0510 (17)	0.0524 (18)	0.0395 (15)	0.0046 (15)	0.0262 (14)	−0.0127 (13)
C1	0.0350 (15)	0.0460 (18)	0.0587 (19)	0.0043 (14)	0.0144 (14)	−0.0056 (14)

Geometric parameters (Å, °)

Ni1—O2^i	1.9849 (16)	C3—C5	1.507 (3)
Ni1—O2	1.9849 (16)	C3—H3A	0.96
Ni1—O3	2.0159 (15)	C3—H3B	0.96
Ni1—O3^i	2.0159 (15)	C3—H3C	0.96
Ni1—O1^i	2.1255 (18)	C10—C9	1.321 (3)
Ni1—O1	2.1255 (18)	C10—C4	1.487 (4)
S1—O1	1.5211 (17)	C8—C9	1.447 (3)
S1—C2	1.775 (3)	C9—H9	0.93
S1—C1	1.780 (3)	C2—H2A	0.96
O5—C10	1.371 (3)	C2—H2B	0.96
O5—C7	1.398 (3)	C2—H2C	0.96
O2—C8	1.262 (3)	C4—H4A	0.96
O3—C5	1.250 (3)	C4—H4B	0.96
O4—C7	1.215 (3)	C4—H4C	0.96
C6—C8	1.440 (3)	C1—H1A	0.96
C6—C7	1.441 (3)	C1—H1B	0.96
C6—C5	1.443 (3)	C1—H1C	0.96
O2^i—Ni1—O2	180	C9—C10—C4	127.3 (2)
O2^i—Ni1—O3	92.94 (6)	O5—C10—C4	111.1 (2)
O2—Ni1—O3	87.06 (6)	O2—C8—C6	125.9 (2)
O2^i—Ni1—O3^i	87.06 (6)	O2—C8—C9	116.6 (2)
O2—Ni1—O3^i	92.94 (6)	C6—C8—C9	117.4 (2)

O3—Ni1—O3[i]	180.0000 (10)	C10—C9—C8	121.6 (2)
O2[i]—Ni1—O1[i]	89.72 (7)	C10—C9—H9	119.2
O2—Ni1—O1[i]	90.28 (7)	C8—C9—H9	119.2
O3—Ni1—O1[i]	89.31 (7)	O3—C5—C6	123.2 (2)
O3[i]—Ni1—O1[i]	90.69 (7)	O3—C5—C3	114.3 (2)
O2[i]—Ni1—O1	90.28 (7)	C6—C5—C3	122.51 (19)
O2—Ni1—O1	89.72 (7)	S1—C2—H2A	109.5
O3—Ni1—O1	90.69 (7)	S1—C2—H2B	109.5
O3[i]—Ni1—O1	89.31 (7)	H2A—C2—H2B	109.5
O1[i]—Ni1—O1	180	S1—C2—H2C	109.5
O1—S1—C2	105.60 (12)	H2A—C2—H2C	109.5
O1—S1—C1	105.41 (12)	H2B—C2—H2C	109.5
C2—S1—C1	97.65 (15)	O4—C7—O5	112.9 (2)
C10—O5—C7	121.85 (18)	O4—C7—C6	128.7 (2)
S1—O1—Ni1	116.97 (9)	O5—C7—C6	118.4 (2)
C8—O2—Ni1	129.32 (15)	C10—C4—H4A	109.5
C5—O3—Ni1	131.49 (15)	C10—C4—H4B	109.5
C8—C6—C7	118.8 (2)	H4A—C4—H4B	109.5
C8—C6—C5	121.45 (19)	C10—C4—H4C	109.5
C7—C6—C5	119.74 (19)	H4A—C4—H4C	109.5
C5—C3—H3A	109.5	H4B—C4—H4C	109.5
C5—C3—H3B	109.5	S1—C1—H1A	109.5
H3A—C3—H3B	109.5	S1—C1—H1B	109.5
C5—C3—H3C	109.5	H1A—C1—H1B	109.5
H3A—C3—H3C	109.5	S1—C1—H1C	109.5
H3B—C3—H3C	109.5	H1A—C1—H1C	109.5
C9—C10—O5	121.6 (2)	H1B—C1—H1C	109.5

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···O4[ii]	0.96	2.55	3.384 (4)	145
C2—H2B···O4[ii]	0.96	2.53	3.370 (4)	146
C2—H2C···O2[iii]	0.96	2.46	3.378 (4)	160

Symmetry codes: (ii) $x+1$, $-y+3/2$, $z+1/2$; (iii) x, $y+1$, z.

Fig. 1

Fig. 2