

Bis(acesulfamato- κO^4)diaquabis-(3-methylpyridine- κN)nickel(II)

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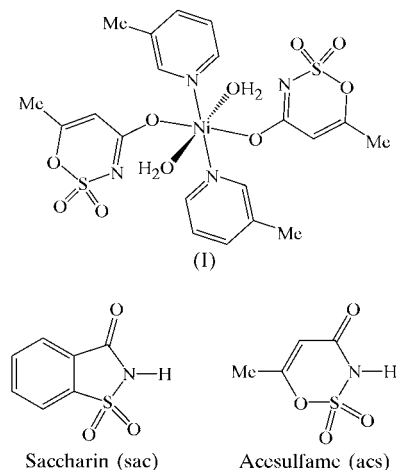
In the crystal structure of the title compound [systematic name: diaquabis(6-methyl-2,2-dioxo-1,2,3-oxathiazin-4-olato- κO^4)bis(3-methylpyridine- κN)nickel(II)], $[\text{Ni}(\text{C}_4\text{H}_4\text{NO}_4\text{S})_2(\text{C}_6\text{H}_7\text{N})_2(\text{H}_2\text{O})_2]$, the Ni^{II} centre resides on a centre of symmetry and has a distorted octahedral geometry. The basal plane is formed by two carbonyl O atoms of two monodentate *trans*-oriented acesulfamate ligands and two *trans* aqua ligands. The axial positions in the octahedron are occupied by two N atoms of two *trans* pyridine ligands. Molecules are stacked in columns running along the *a* axis. There are π - π stacking interactions between the molecules in each column, with a distance of 3.623 (2) Å between the centroids of the pyridine rings. There are also O—H \cdots O interactions between the columns.

Comment

Acesulfame is an oxathiazinone dioxide and is systematically named as 6-methyl-1,2,3-oxathiazin-4(3*H*)-one 2,2-dioxide; it is also known as 6-methyl-3,4-dihydro-1,2,3-oxathiazin-4-one 2,2-dioxide or acetosulfam. It was discovered by the chemist Karl Clauss in 1967 (Clauss & Jensen, 1973) and has been widely used as a non-caloric artificial sweetener since 1988, after the US Food and Drug Administration granted approval (Duffy & Anderson, 1998). Many countries have approved the use of acesulfame K, *viz.* the potassium salt of acesulfame, in soft drinks, candies, toothpastes, mouthwashes, cosmetics and pharmacological preparations (Mukherjee & Chakrabarti, 1997).

The acesulfamate anion (acs^-) has several potential donor atoms and thus, as a polyfunctional ligand, it can engage in N, O_{CO} , O_{OSO} or O coordination with different metal ions, similar to the saccharinate anion (sac). The chemistry of the common artificial sweetener acesulfame (acs) is an interesting area of research not only because of its biological significance but also because of its coordination properties. Despite its potential for diversity in coordination, little has been reported on the coordination behaviour of acesulfamate as a ligand. Recently,

we have started to study the synthesis and the spectroscopic and structural properties of acesulfamate metal complexes (İçbudak, Heren *et al.*, 2005; İçbudak, Bulut *et al.*, 2005; Bulut *et al.*, 2005; İçbudak *et al.*, 2006; Dege *et al.*, 2006). The donor sites of the acesulfamate ligand are similar to those of the saccharinate anion (see scheme above), and therefore the coordination behaviour of the title compound, (I), can be



compared with the coordination chemistry of saccharin, since all possible bonding patterns of saccharin are well documented by X-ray diffraction studies (İçbudak *et al.*, 2002, and references therein). In order to examine the coordination behaviour of acesulfame in transition metal complexes, the title complex, (I), has been synthesized and its crystal structure is presented here.

A view of the molecule of (I), together with the atom-numbering scheme and the intramolecular hydrogen bonding, are shown in Fig. 1. Selected geometric parameters are listed in Table 1. The structure is composed of discrete $[\text{Ni}(\text{acs})_2-$

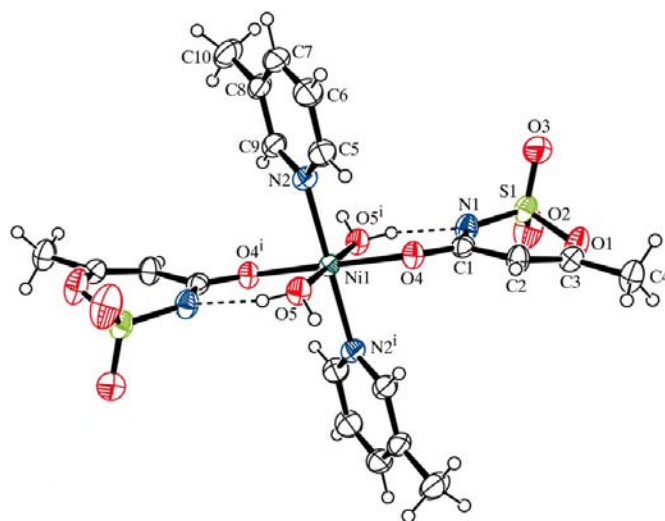


Figure 1

A view of the title molecule, showing the atom-labelling scheme and 40% probability displacement ellipsoids. Intramolecular O—H \cdots N hydrogen bonds are represented as dashed lines. [Symmetry code: (i) $-x + 1, -y, -z$.]

(mepyr)₂(H₂O)₂ molecules (mepyr is 3-methylpyridine). The local structure around the Ni^{II} ion, which resides on a centre of symmetry, is that of an octahedron, of which the equatorial plane [O4/O5/O4ⁱ/O5ⁱ; symmetry code: (i) $-x + 1, -y, -z$] is formed by two carbonyl O atoms of two *trans*-oriented acesulfamate ligands (O4 and O4ⁱ) and two *trans* aqua ligands (O5 and O5ⁱ). The axial positions in the octahedron are occupied by two N atoms of two *trans* pyridine ligands (N2 and N2ⁱ). The bond lengths and angles of the acesulfamate ligands are similar to the corresponding values of the copper(II)-acesulfamate complex [Cu(acs)₂(mepyr)₂] (Dege *et al.*, 2006), while there are some differences from the analogous potassium salt (Paulus, 1975). The most pronounced of these are the S1–N1 bond length and O2=S1=O3 angle, which are increased to 1.571 (2) Å and 116.45 (15)°, respectively, in (I), from corresponding values of 1.544 (2) Å and 113.7 (2)°, respectively, in the potassium salt. The acesulfame ring adopts a half-chair conformation, as is evident from the puckering parameters [$Q = 0.305$ (2) Å, $\theta = 60.5$ (4)° and $\varphi = 11.2$ (5)° for the atom sequence S1–O1–C3=C2–C1=N1 (Cremer & Pople, 1975)]. The mepyr ligands are planar. Their individual bond lengths do not depart significantly from their respective mean values and correspond well to those reported for this ligand in other complexes (Rotondo, 2006; Goto *et al.*, 2000; Nakagawa *et al.*, 2000).

The most relevant aspect of this structure is the carbonyl O-atom coordination of the acesulfamate anions, since the acesulfamate ligand coordinates to the metal(II) ion through the ring N atom in [Co(acs)₂(H₂O)₄] (İçbudak, Bulut *et al.*, 2005) and is coordinated in a bidentate manner to the metal(II) ion in [Cu(acs)₂(ampym)₂] (ampym is aminopyrimidine; Bulut *et al.*, 2005) and [Cu(acs)₂(mepyr)₂] (Dege *et al.*, 2006). Apart from considering the structural resemblance of acesulfame to saccharin, it can also be said that this coordination

behaviour is very interesting since saccharin usually interacts with metal atoms through its deprotonated N atom (Haider *et al.*, 1985). This unusual carbonyl coordination of saccharin was observed in a few cases either in mixed ligand complexes of saccharin {[Ni(sac)₂(py)₄]-2py; py is pyridine; İçbudak *et al.*, 2002} or in trivalent lanthanide- and yttrium-saccharinate complexes (Piro *et al.*, 2002). In the former case, the carbonyl O-atom coordination was attributed to the steric effect, while in the latter case, the heavy metal ion affects the coordination mode. Nevertheless, none of these reasons can be adopted for carbonyl O-atom coordination of the acesulfamate ligand to the nickel(II) ion.

When the local structure around the Ni^{II} ion in (I) is compared with that in [Ni(acs)₂(H₂O)₄] (İçbudak *et al.*, 2006), one can observe that the Ni–O_{acs} distance of 2.0747 (15) Å in (I) is almost equal to that in [Ni(acs)₂(H₂O)₄] [2.0689 (11) Å], while the Ni–O_{aqua} distance of 2.0917 (16) Å in (I) is longer than the two Ni–O_{aqua} distances of 2.0481 (13) and 2.0568 (11) Å in [Ni(acs)₂(H₂O)₄]. The angular distortions of the octahedral environment of the Ni^{II} ion in (I) also show some differences from those in the [Ni(acs)₂(H₂O)₄] complex. The maximum deviation from an ideal O–M–O angle of 90° is 3.87 (7)° for (I), while it is 5.09 (5)° for the [Ni(acs)₂(H₂O)₄] complex. With regard to the ligand geometry, the C–O bond length of the carbonyl group is increased by 0.017 Å in (I) compared with that in the potassium salt, whereas no significant changes are observed for the sulfonyl group. The bond lengths of these groups are especially important for IR studies, from which the coordination behaviour of the ligand (Grupce *et al.*, 2001; Naumov *et al.*, 2001) can be estimated.

On the basis of the estimated 'effective' ionic radii for Cu²⁺ (0.73 Å) and Ni²⁺ (0.69 Å) in a six-coordinate environment (Shannon, 1976), the corresponding M–N_{mepyr} bond distance in (I) and [Cu(acs)₂(mepyr)₂] (Dege *et al.*, 2006) would be expected to be fairly similar in magnitude. This premise is clearly not supported by a comparison of the M–N_{mepyr} bond distances in the two complexes. In terms of the M–N_{mepyr} distance, the Ni–N distance in (I) is ca 0.09 Å longer than the equivalent Cu–N bond distances in [Cu(acs)₂(mepyr)₂].

In the molecular structure, an intramolecular O5–H5A···N1ⁱ contact (see Table 2 for details and symmetry code) leads to the formation of a six-membered ring, which is fused with the acesulfame ring. In the crystal structure (Fig. 2), molecules of the title compound are packed in columns running along the *a* axis. The molecules in each column are linked to one another in a zigzag arrangement *via* π – π stacking interactions, which takes the form of stacks of pyridine rings. The pyridine rings at (*x*, *y*, *z*) and ($-x$, $-y$, $-z$) have an interplanar spacing of 3.308 (2) Å and a centroid separation of 3.623 (2) Å, corresponding to a ring offset of 1.476 (3) Å. In addition, there are intermolecular O–H···O interactions between the molecules in the 2₁ screw symmetry-related columns. In this interaction, atom O5 acts as a hydrogen-bond donor, *via* atom H5B, to atom O2 at ($-x + 1$, $y + \frac{1}{2}$, $-z - \frac{1}{2}$) (Table 2). There are no other significant intermolecular interactions, such as C–H··· π interactions, in the crystal structure of (I).

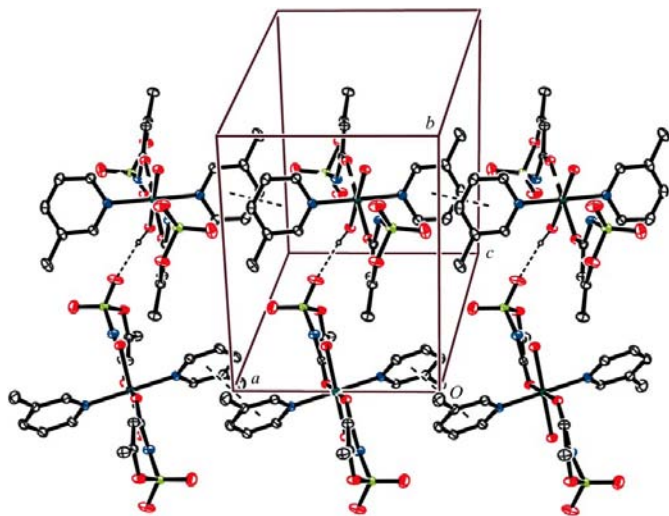


Figure 2
A packing diagram of (I), showing the O–H···O and π – π interactions. For clarity, only H atoms involved in hydrogen bonding have been included.

Experimental

[Ni(acs)₂(H₂O)₄] (0.91 g, 2 mmol) was dissolved in methanol (50 ml) and a solution of 3-methylpyridine (0.37 g, 4 mmol) in methanol (30 ml) was added with stirring. The solution was stirred vigorously for 3 h at 323 K and then cooled to ambient temperature. The resulting blue crystals were washed with acetone and dried under vacuum (yield 90%).

Crystal data

[Ni(C ₄ H ₄ NO ₄ S) ₂ (C ₆ H ₇ N) ₂ (H ₂ O) ₂]	<i>Z</i> = 2
<i>M_r</i> = 605.28	<i>D_x</i> = 1.580 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 8.9738 (6) Å	<i>μ</i> = 0.99 mm ⁻¹
<i>b</i> = 12.8267 (7) Å	<i>T</i> = 296 K
<i>c</i> = 11.1870 (8) Å	Prism, blue
<i>β</i> = 98.875 (5)°	0.46 × 0.28 × 0.09 mm
<i>V</i> = 1272.25 (14) Å ³	

Data collection

Stoe IPDS-2 diffractometer	21143 measured reflections
<i>ω</i> scans	2999 independent reflections
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	2271 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.484, <i>T</i> _{max} = 0.881	<i>R</i> _{int} = 0.063
	<i>θ</i> _{max} = 27.8°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.0532P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.01	$\Delta\rho_{\text{max}} = 0.53 \text{ e } \text{\AA}^{-3}$
2999 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
179 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected bond lengths (Å).

Ni1—O4	2.0747 (15)	O1—C3	1.378 (3)
Ni1—O5	2.0917 (16)	O4—C1	1.256 (3)
Ni1—N2	2.0964 (18)	N1—C1	1.345 (3)
S1—O3	1.412 (2)	C1—C2	1.458 (3)
S1—O2	1.4145 (19)	C2—C3	1.320 (3)
S1—O1	1.6134 (18)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5A...N1 ⁱ	0.83 (4)	1.96 (4)	2.739 (3)	155 (3)
O5—H5B...O2 ⁱⁱ	0.83 (4)	1.96 (4)	2.792 (3)	173 (4)

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

The coordinates of the H atoms of the water molecule were determined from a difference map and were then allowed to refine

isotropically [O—H = 0.83 (4) Å]. All other H atoms were positioned geometrically and refined with a riding model, fixing the bond lengths at 0.93 and 0.96 Å for CH and CH₃ groups, respectively. The *U*_{iso}(H) values were constrained to be 1.2*U*_{eq}(parent) or 1.5*U*_{eq}(methyl C). Riding methyl H atoms were allowed to rotate freely during refinement using the AFIX 137 command of *SHELXL97* (Sheldrick, 1997).

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3023). Services for accessing these data are described at the back of the journal.

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