Diaquabis(pyridine-2-carboxamide-$\kappa^2 N^1, O^2$)nickel(II) disaccharinate tetrahydrate

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In the crystal structure of the title compound, $[Ni(C_6H_6N_2O)_2(H_2O)_2](C_7H_4NO_3S)_2\cdot 4H_2O$ or $[Ni(pia)_2(H_2O)_2](sac)_2\cdot 4H_2O$ (pia is picolinamide or pyridine-2-carboxamide, and sac is the saccharinate anion), the Ni^{2+} cation, located on a centre of symmetry, is coordinated by two symmetry-related aqua ligands together with a pair of symmetry-related bidentate pia molecules and exhibits a distorted octahedral environment. The unique unligated sac anion in the asymmetric unit resides on a general position and has a single negative charge. The coordinated water molecules link the sac ions to the metal complex *via* O—H···O hydrogen bonds. In addition, the sac ions are linked to the metal complex *via* intermolecular π–π interactions between the benzene ring of the sac ion and the pyridine ring of a pia ligand. Each uncoordinated water molecule is hydrogen bonded to sac moieties through O—H···O and O—H···N hydrogen bonds.

Comment

The water-soluble alkali and alkali-earth salts of saccharinate (sac) are widely used as non-caloric artificial sweeteners and food additives; neutral saccharin itself does not coordinate to metal ions, but its deprotonated form (sac) interacts with trace elements in the human body and readily forms complexes with a large number of metal ions (Andaç *et al.*, 2000; Zhang, 1994). The sac anion can bind metal centres through different donor atoms, for example, the endocyclic N and the exocyclic carbonyl or sulfonyl O atoms. A large number of crystal structures of sac compounds have revealed a variety of metal-bonding patterns for sac (Naumov *et al.*, 2001; Icbudak *et al.*, 2001), including (in order of observed frequency) monofunctional bonding to the deprotonated ring N atom, bifunctional amidate bridging through N and carbonyl O atoms, bifunctional chelation to N and carbonyl O atoms, monofunctional bonding to carbonyl O atoms, and trifunctional binding to N, carbonyl O and sulfonyl O atoms. Furthermore, sac molecules

exist very often in a free ionic form, *i.e.* without metal bonding (Icbudak *et al.*, 2001; Naumov *et al.*, 2001; Çakır *et al.*, 2003; Castellano *et al.*, 2002), or quite rarely as a neutral form without metal bonding in a sac salt (Deng *et al.*, 2001). Aqua complexes of sac with transition metals and inner transition metals have been reported (Haider *et al.*, 1983; Kamenar & Jovanovski, 1982). The syntheses and structural and thermal characterizations of mixed-ligand metal complexes of sac alongside mono- and bidentate N-donor ligands, such as pyridine (Magri *et al.*, 1980; Quinzani *et al.*, 1997, 1999; Jovanovski *et al.*, 1998), imidazole (Jianmin *et al.*, 1992, 1997), phenanthroline (Deng *et al.*, 2000; Baran *et al.*, 2000) and monoethanolamine (Andaç *et al.*, 2000), have been reported in the literature. A series of mixed-ligand sac complexes of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} with nicotinamide have also been reported (Çakır *et al.*, 2003; Castellano *et al.*, 2002).

(I)
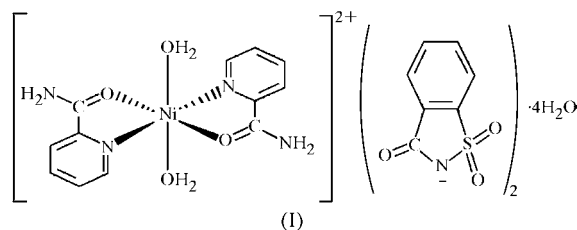
Picolinamide (pia) ligands represent a promising class of bidentate complexing molecules that can be used to separate trivalent actinide and/or lanthanide cations from aqueous solutions of nuclear waste obtained by dissolution of spent fuel in nitric acid. These ligands possess such functionality because they combine a moderately hard amide O- and a softer pyridine N-binding site, which can co-operatively bind hard cations with possible discrimination as a function of size and hardness (Beaden *et al.*, 2003). We describe here the coordination behaviour of pia, an isomer of nicotinamide, in a nickel complex that crystallizes with saccharinate as counter-anion.

Fig. 1 shows an *ORTEP*-3 plot (Farrugia, 1997) of (I). The Ni^{II} ion is located on a centre of symmetry, chelated by two pia molecules. Pia acts as an *N,O*-bidentate ligand and forms the
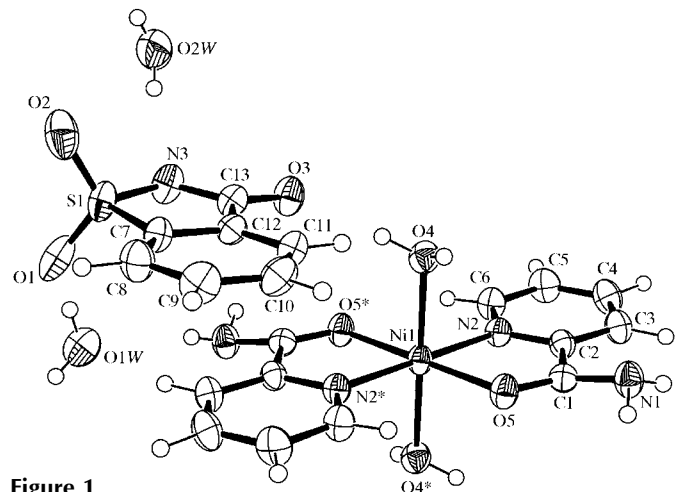

Figure 1
The molecular structure of (I). Atoms marked with an asterisk (*) are at the symmetry position $(-x, 1-y, 1-z)$.

equatorial plane of the coordination octahedron, while the water molecule occupies the axial position. The Ni—N distance is 2.0343 (13) Å and the Ni—O distances are 2.0301 (12) and 2.1297 (13) Å (Table 1). These values are as expected and are comparable to those observed in the Ni–nicotinamide complex (Çakır et al., 2003). The unique sac anion in the asymmetric unit carries a single negative charge and acts as a counter-anion. The sac groups are essentially planar. The mean plane through the sac anion is almost parallel [dihedral angle = 7.16 (2)°] to that through the pia moiety.

In the extended structure of (I), shown in Fig. 2, there are weak intermolecular π–π and π–ring interactions. An intermolecular π–π interaction occurs between the benzene rings of the sac groups (hereafter A) of neighbouring molecules. Ring A is oriented in such a way that the perpendicular distance from A to A^v is 3.399 Å, the closest distance being C7···C10^v [3.692 (4) Å; symmetry code: (v) $1 - x, 1 - y, -z$]. The distance between the ring centroids is 3.6976 (12) Å. An inhomogeneous arrangement of π electron density through the benzene ring is probably responsible for the mutual orientation of the benzene rings and the π–π interaction being of the parallel-displaced (PD) type (Kamishima et al., 2001). Furthermore, ring A also forms an intermolecular π–π contact with the pyridine ring (B) of the picolinamide. Rings A and B are oriented in such a way that the perpendicular distance from A to B is 3.51 Å, the closest interatomic distance being C2···C12 [3.574 (2) Å], and the dihedral angle between the planes of rings A and B is 6.75 (13)°. The distance between the ring centroids is 3.7147 (11) Å. Ring B is also involved in intermolecular O—H···π interactions with a free water molecule, with the following geometrical parameters: (i) the distance between atom H1W (bonded to O1W) and the centre of ring B is 3.25 (7) Å; (ii) the distance between atom H1W and the plane of ring B is 2.99 Å; (iii) the angle between the line connecting atom H1W to the centre of ring B, CgB, and
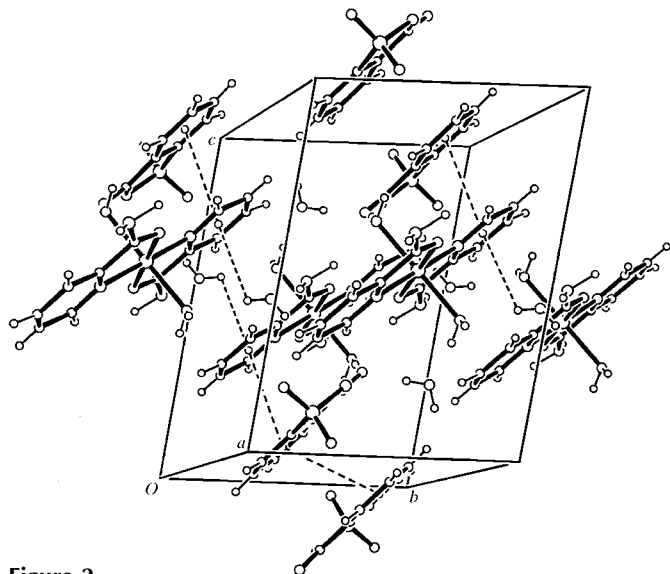
the normal to the plane of B is 23.13°; (iv) the O1W—H1W···CgB angle is 95 (6)°. These interactions are shown with dashed lines in Fig. 2. The coordinated water molecules link the sac ion to the metal complex via O4—H7···O3 hydrogen bonds (Fig. 1). One unligated water molecule (O1W) is hydrogen bonded to the sac ion (O1W—H2W···O1) and to the coordinated water molecule (O1W—H1W···O4^{iv}). The other uncoordinated water molecule (O2W) is hydrogen bonded to the sac ion (O2W—H4W···N3 and O2W—H3W···O2^i; symmetry codes as in Table 2). The other hydrogen bonds are listed in Table 2. This varied set of hydrogen-bonding, π–π and π–ring interactions employs most of the available topological features to stabilize the crystal structure.

Experimental

A solution of pia (0.244 g, 2 mmol) in ethanol (30 ml) was added dropwise with stirring to a solution of nickel saccharinate (0.530 g, 1 mmol) in hot water (50 ml). The mixture was heated (to 353 K) in a temperature-controlled bath with stirring for 2 h. The resulting blue solution was evaporated at room temperature, yielding blue crystals suitable for X-ray diffraction analysis.

Crystal data

[Ni(C6H6N2O)2(H2O)2]-(C7H4NO3S)2·4H2O	$Z = 1$
$M_r = 775.41$	$D_x = 1.613$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.4478$ (7) Å	Cell parameters from 13 935
$b = 8.8751$ (7) Å	reflections
$c = 12.3854$ (9) Å	$\theta = 2.6–29.0°$
$\alpha = 81.560$ (6)°	$\mu = 0.82$ mm^{-1}
$\beta = 72.655$ (6)°	$T = 293$ (2) K
$\gamma = 64.257$ (6)°	Plate, blue
$V = 798.24$ (11) Å^3	$0.35 \times 0.28 \times 0.15$ mm

Data collection

Stoe IPDS-II diffractometer	4243 independent reflections
ω scans	3267 reflections with $I > 2\sigma(I)$
Absorption correction: by integration (X-RED32; Stoe & Cie, 2002)	$R_{int} = 0.061$
	$\theta_{max} = 29.0°$
	$h = -11 \rightarrow 11$
$T_{min} = 0.661, T_{max} = 0.828$	$k = -12 \rightarrow 12$
18 441 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.034$	
$wR(F^2) = 0.092$	
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2]$
4207 reflections	where $P = (F_o^2 + 2F_c^2)/3$
287 parameters	$(\Delta/\sigma)_{max} = 0.044$
	$\Delta\rho_{max} = 0.31$ e Å^{-3}
	$\Delta\rho_{min} = -0.63$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O5	2.0301 (12)	O5—C1	1.248 (2)
Ni1—N2	2.0343 (13)	O3—C13	1.250 (2)
Ni1—O4	2.1297 (13)	N2—C6	1.331 (2)
S1—O2	1.4349 (16)	N2—C2	1.344 (2)
S1—O1	1.4393 (17)	N1—C1	1.313 (2)
O5—Ni1—N2	80.05 (5)	C6—N2—C2	119.43 (14)
O5—Ni1—O4	89.14 (6)	C2—N2—Ni1	114.30 (11)
N2—Ni1—O4	89.17 (5)	C13—N3—S1	110.76 (13)
O2—S1—O1	114.08 (10)	O5—C1—N1	121.89 (17)
C1—O5—Ni1	114.74 (11)	N2—C6—C5	121.79 (17)

Figure 2
The crystal packing of (I). Dashed lines denote intermolecular π–π and π–ring interactions.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O4-H8 \cdots O2W^{i}$	0.89 (4)	1.87 (4)	2.751 (2)	171 (3)
$N1-H1 \cdots O3^{i}$	0.87 (3)	2.11 (3)	2.951 (2)	161 (2)
$N1-H2 \cdots O1W^{ii}$	0.82 (3)	2.16 (3)	2.971 (3)	166 (3)
$O2W-H3W \cdots O2^{iii}$	0.83 (4)	2.11 (4)	2.929 (2)	168 (4)
$O1W-H1W \cdots O4^{iv}$	0.80 (2)	2.16 (2)	2.956 (2)	173 (7)
$O2W-H4W \cdots N3$	0.80 (4)	2.22 (4)	3.004 (3)	164 (4)
$O4-H7 \cdots O3$	0.87 (3)	1.92 (3)	2.7923 (19)	175 (3)
$O1W-H2W \cdots O1$	0.81 (6)	2.34 (5)	2.940 (3)	132 (6)

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

Atoms H3W and H4W, bonded to O2W, were found in a difference map and their parameters were refined with the O—H distance restrained to 0.82 (2) Å. The other H atoms were located in a difference Fourier map and their coordinates and U_{iso} parameters were refined freely [O—H = 0.80 (2)–0.89 (4) Å, N—H = 0.82 (3) and 0.87 (3) Å and C—H = 0.88 (3)–1.00 (2) Å].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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