Table 2. *Selected geometric parameters* (Å, °)

Pd—Cl	2.289 (2)	C(11)—C(12)	1.382 (7)
Pd—P	2.324 (2)	C(11)—C(16)	1.392 (7)
P—N	1.727 (6)	C(12)—C(13)	1.391 (9)
P—C(11)	1.794 (5)	C(13)—C(14)	1.36 (1)
N—C(1)	1.425 (7)	C(14)—C(15)	1.358 (9)
C(1)—C(2)	1.461 (9)	C(15)—C(16)	1.402 (9)
C(2)—C(3)	1.460 (9)		
P—Pd—Cl	90	C(2)—C3—C(2i)	114.0 (8)
Pd—P—N	108.6 (2)	P—C(11)—C(12)	119.2 (4)
Pd—P—C11	118.7 (2)	P—C(11)—C(16)	121.1 (4)
N—P—C(11)	104.1 (2)	C(12)—C(11)—C(16)	119.2 (5)
C(11)—P—C(11i)	100.9 (3)	C(11)—C(12)—C(13)	119.3 (5)
P—N—C(1)	118.1 (4)	C(12)—C(13)—C(14)	120.8 (6)
C(1)—N—C(1i)	113.4 (7)	C(13)—C(14)—C(15)	120.5 (6)
N—C(1)—C(2)	113.5 (6)	C(14)—C(15)—C(16)	119.6 (6)
C(1)—C(2)—C(3)	114.1 (6)	C(11)—C(16)—C(15)	119.9 (5)

Symmetry code: $x, y, -z$.

Table 3. *A comparison of the molecular geometry of the piperidine ring determined in this paper to those of free piperidine* (*Koman, Durcanska, Handlovic & Gazo,* 1983) *and two tri(piperidino)phosphine molecules* (*Rømming & Sonstad,* 1978)

Piperidine group 1 has the P-atom lone pair *anti* to the N-atom lone pair; groups 2 and 3 are *gauche*; the estimated standard deviations are given in parentheses following the values.

	P—N bond length (Å)	C(1)—N—C(5) angle (°)	Sum of angles about the N atom (°)	Sum of absolute values of torsion angles of the C and N atoms of the piperidine ring (°)
Free ligand		112.0		345.6
Tri(piperidino)-phosphine I, group 1	1.727 (3)	109.9 (3)	339.6 (5)	347.0 (10)
Tri(piperidino)-phosphine I, group 2	1.692 (3)	112.9 (3)	359.9 (5)	331.3 (10)
Tri(piperidino)-phosphine I, group 3	1.705 (3)	112.1 (3)	350.4 (5)	337.4 (10)
Tri(piperidino)-phosphine II, group 1	1.724 (3)	109.8 (3)	338.9 (5)	348.8 (10)
Tri(piperidino)-phosphine II, group 2	1.689 (3)	112.5 (3)	359.6 (5)	333.8 (10)
Tri(piperidino)-phosphine II, group 3	1.708 (3)	111.9 (3)	349.9 (5)	338.0 (10)
This paper	1.727 (6)	113.4 (7)	349.6 (9)	279.6 (16)

Systematic absences: $0kl$ if $k + l = 2n + 1$, $h0l$ if $h + l = 2n + 1$. The structure was solved by the heavy-atom method. A difference map showed maxima in positions consistent with the expected locations of the H atoms. In the final round of calculations the H atoms were positioned on geometric grounds (C—H = 0.96 Å) and included (as riding atoms) in the structure-factor calculations. The H atoms were assigned general isotropic displacement parameters ($U_{\rm iso}$ = 0.08 Å^2). All calculations were carried out on a PDP11/23 computer using *SDP* (B. A. Frenz & Associates, Inc., 1982), a DSP10020 computer using *SHELXS*86 (Sheldrick, 1985) and on a personal computer using *SHELXTL/PC* (Sheldrick, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71508 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1043]

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Pentaaqua(2-furancarboxylato)nickel(II) 2-Furancarboxylate at 120 K

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Abstract

The crystal structure of [Ni($C_5H_3O_3$)(H_2O)$_5$]($C_5H_3O_3$) has been determined by X-ray diffraction at 120 K. One 2-furancarboxylate anion and five water molecules are in-

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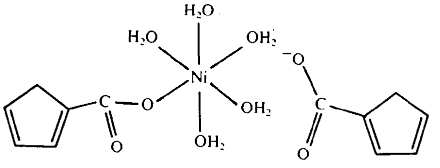
volved in formation of a distorted octahedron around the Ni atom. The Ni—O bond lengths range from 2.019 (3) to 2.090 (3) Å. The second anion is linked to the complex cation by bifurcated hydrogen bonds. There is no significant difference between the geometries of the coordinated and uncoordinated anions.

Comment

A variety of coordination schemes have been reported for complexes of 2-furancarboxylic acid with the uranyl ion, lanthanide ions, copper(II) and silver(I) ions. Uranyl ions are present as hydroxo-bridged dimers linked through carboxylate ligands to form infinite chains (Alcock, Kemp & Leciejewicz, 1991). In erbium and yttrium furoates the 2-furancarboxylate anions are bonded as bidentate bridging *O*:*O′* ligands (Kozioł, Brzyska, Klimek, Król & Stepniak, 1987). Pr^{3+} coordinates two O atoms from a bidentate furoate anion and bonds other carboxylate ions as bi- and terdentate bridging ligands (Kozioł, Brzyska, Klimek, Król, Palenik & Stepniak, 1989). In the copper compound, two Cu^{2+} ions form a dimer bridged by O atoms belonging to four bidentate furoate anions (Charbonnier, Petit-Ramel, Faure & Loiseleur, 1984). In the structure of the silver furoate (Charbonnier, Petit-Ramel, Faure & Loiseleur, 1984), a three-dimensional polymer is composed of five-coordinate silver(I) cations and bridging tetradentate *O*,*O′*:*O*,*O′* furoate anions. We therefore considered it interesting to examine the crystal structures of furoic acid complexes with some other metal ions. The crystal and molecular structure of nickel furoate (I) is presented in this paper.



(I)

The title structure consists of two discrete units: pentaaqua(2-furancarboxylato)nickel(II) cations and 2-furancarboxylate anions. In the complex cation, Ni^{2+} binds only one furancarboxylate ligand in a monodentate mode. The second anion is bonded to the cation *via* hydrogen bonds only (Fig. 1). A comparison between the intraligand distances and angles in coordinated and hydrogen-bonded anions does not indicate any significant differences. Moreover, the geometry of both anions is similar, within the e.s.d.'s, to that calculated for the free 2-furancarboxylic acid (Gilmore, Mallinson & Speakman, 1983). The magnitudes of the bond angles O3—C2—C1 (119.5°) and C3—C2—C1 (128.3°), and correspondingly in the second anion O6—C7—C6 (115.4°) and C8—C7—C6 (134.6°), suggest the conjugative interaction between the O atom from the heterocyclic ring and O atoms from the carboxylate group, which was reported by John, Ritchie & Radom (1977). A similar interesting feature of the same carboxylate species, both coordinated and ionic, was observed by Smith, O'Reilly & Kennard (1982) in the cases of pentaaqua(2,4,5-trichlorophenoxyacetato)manganese(II) 2,4,5-trichlorophenoxyacetate and pentaaqua(2,4,5-trichlorophenoxyacetato)magnesium(II) 2,4,5-trichlorophenoxyacetate. In these cases, however, the stability of the complex was maintained by the presence of π-π interactions with the 2,4,5-trichlorophenoxyacetate rings. Since the title complex exhibits nearly orthogonal alignment of the furan rings [81.2 (1)°], π-π charge-transfer interactions are excluded. The existence of two discrete ions with interionic contacts within normal van der Waals distances seems, therefore, to be only an effect of the packing in the system (Fig. 2). All the water ligands are engaged in formation of inter- and intramolecular hydrogen bonds (Table 3).

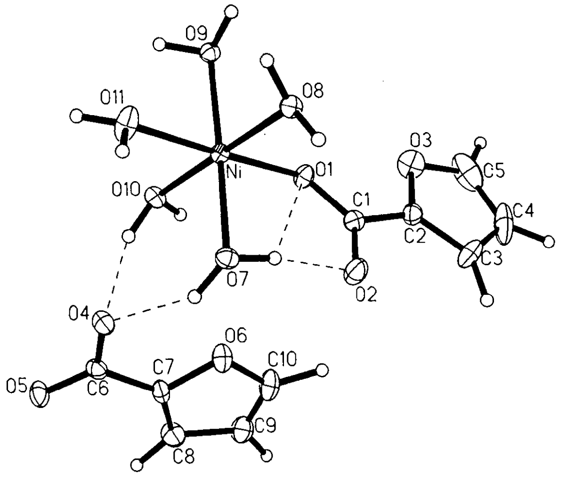


Fig. 1. View of pentaaqua(2-furancarboxylato)nickel(II) 2-furancarboxylate showing the labelling of the non-H atoms.

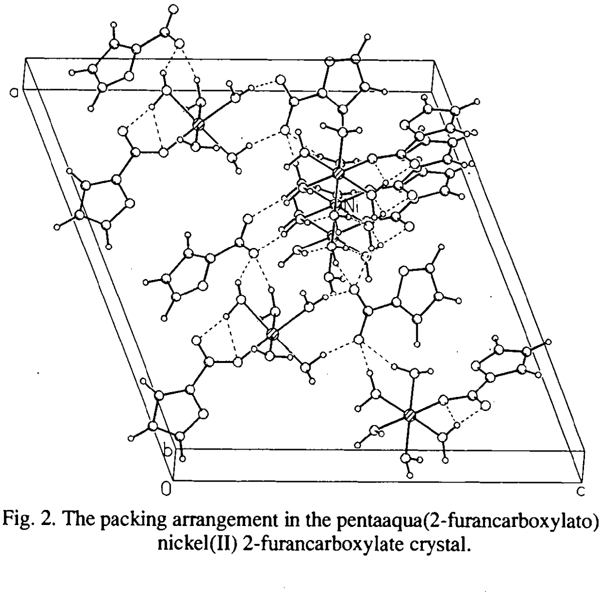


Fig. 2. The packing arrangement in the pentaaqua(2-furancarboxylato)nickel(II) 2-furancarboxylate crystal.

This results in the formation of cyclic hydrogen-bonded dimers in the *ac* plane of the crystal. Two water molecules are involved as donors in two bifurcated hydrogen bonds between O7—H71···O1 and O7—H71···O2, and O8—H82···O5 and O8—H82···O9. The relatively short Ni—O1 distance of 2.019 (3) Å compared to the Ni—O(aqua) distances suggests that the coordinated ligand is strongly bonded to the electropositive ion.

Experimental

The title compound was prepared by the reaction of a warm aqueous solution of 2-furancarboxylic acid with nickel(II) carbonate. The green needle-shaped crystals were obtained after a few days of slow evaporation at room temperature.

Crystal data (at 290 K in square brackets)

$[Ni(C_5H_3O_3)(H_2O)_5](C_5H_3O_3)$
M_r = 370.94
Monoclinic
$C2$
a = 18.150 (9) [18.346 (9)] Å
b = 4.849 (2) [4.908 (3)] Å
c = 17.418 (9) [17.508 (8)] Å
β = 110.58 (7) [111.11 (5)]°
V = 1435.1 (14) [1470.7 (15)] Å^3
Z = 4
D_x = 1.717 (3) [1.675 (3)] Mg m^{-3}

D_m = [1.66] Mg m^{-3}
D_m measured by flotation in CH_3Cl/CH_2BrCH_2Br
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 9-12°
μ = 1.41 [1.38] mm^{-1}
T = 120.0 (5) [290 (1)] K
Needle
0.2 × 0.15 × 0.1 mm
Green

Data collection

Kuma KM-4 computer-controlled four-circle κ-axis diffractometer
$\omega/2\theta$ scans
Absorption correction: *DIFABS* (Walker & Stuart, 1983)
T_{min} = 0.93, T_{max} = 1.03
2888 measured reflections
2888 independent reflections

1942 observed reflections [$F > 6\sigma(F)$]
θ_{max} = 32.5°
$h = 0 \rightarrow 27$
$k = 0 \rightarrow 7$
$l = -26 \rightarrow 23$
3 standard reflections monitored every 100 reflections intensity variation: 3%

Refinement

Refinement on F
R = 0.0327
wR = 0.0328
S = 1.55
1942 reflections
244 parameters
Calculated weights $w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{max}$ = 0.34
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0.66808 (3)	0.5	0.63933 (3)	0.01191 (8)
O1	0.72319 (17)	0.2870 (7)	0.74336 (17)	0.0165 (6)
O2	0.68969 (17)	0.5461 (8)	0.83332 (17)	0.0233 (8)
O3	0.83252 (19)	0.0160 (15)	0.86520 (20)	0.0298 (7)
O4	0.45391 (16)	0.4340 (7)	0.60622 (17)	0.0175 (6)
O5	0.34448 (16)	0.1835 (8)	0.57862 (17)	0.0219 (7)
O6	0.52048 (17)	0.2056 (8)	0.75292 (18)	0.0213 (6)
O7	0.59672 (16)	0.7092 (7)	0.69170 (17)	0.0157 (6)
O8	0.74928 (17)	0.8068 (7)	0.67850 (18)	0.0149 (6)
O9	0.73711 (17)	0.3014 (7)	0.58282 (17)	0.0149 (6)
O10	0.58550 (17)	0.1857 (7)	0.60061 (18)	0.0156 (6)
O11	0.61448 (21)	0.7001 (8)	0.53146 (19)	0.0243 (8)
C1	0.72910 (23)	0.3601 (9)	0.81589 (24)	0.0157 (8)
C2	0.78753 (23)	0.2096 (10)	0.88284 (24)	0.0179 (8)
C3	0.80603 (29)	0.2429 (12)	0.96527 (25)	0.0263 (11)
C4	0.86604 (31)	0.0461 (16)	1.00095 (29)	0.0436 (16)
C5	0.88108 (32)	−0.0845 (13)	0.94010 (38)	0.0411 (14)
C6	0.41157 (23)	0.2585 (11)	0.62496 (22)	0.0157 (8)
C7	0.44405 (23)	0.1312 (10)	0.70693 (24)	0.0171 (8)
C8	0.41680 (25)	−0.0532 (10)	0.74890 (27)	0.0247 (11)
C9	0.47894 (27)	−0.0963 (13)	0.82525 (27)	0.0284 (11)
C10	0.53887 (27)	0.0604 (11)	0.82426 (25)	0.0288 (12)

Table 2. *Selected geometric parameters* (Å, °)

O1—Ni	2.019 (3)	C6—O5	1.255 (5)
O7—Ni	2.090 (3)	C7—O6	1.384 (5)
O8—Ni	2.035 (3)	C10—O6	1.364 (5)
O9—Ni	2.082 (3)	C2—C1	1.465 (6)
O10—Ni	2.077 (3)	C3—C2	1.364 (5)
O11—Ni	2.033 (3)	C4—C3	1.417 (8)
C1—O1	1.280 (5)	C5—C4	1.342 (8)
C1—O2	1.253 (6)	C7—C6	1.475 (6)
C2—O3	1.349 (7)	C8—C7	1.354 (6)
C5—O3	1.381 (7)	C9—C8	1.425 (6)
C6—O4	1.264 (5)	C10—C9	1.332 (8)
O7—Ni—O1	92.5 (2)	O2—C1—O1	125.6 (4)
O8—Ni—O1	90.1 (2)	C2—C1—O1	115.7 (4)
O9—Ni—O1	89.8 (2)	C2—C1—O2	118.7 (4)
O10—Ni—O1	89.4 (2)	C1—C2—O3	119.5 (5)
O11—Ni—O1	177.1 (2)	C3—C2—O3	112.2 (5)
O8—Ni—O7	89.2 (2)	C3—C2—C1	128.3 (5)
O9—Ni—O7	177.6 (2)	C4—C3—C2	104.4 (5)
O10—Ni—O7	90.6 (2)	C5—C4—C3	108.0 (6)
O11—Ni—O7	90.2 (2)	C4—C5—O3	109.9 (6)
O9—Ni—O8	90.7 (2)	O5—C6—O4	124.7 (4)
O10—Ni—O8	179.4 (2)	C7—C6—O4	117.4 (4)
O11—Ni—O8	90.9 (2)	C7—C6—O5	117.9 (4)
O10—Ni—O9	89.6 (2)	C6—C7—O6	115.4 (4)
O11—Ni—O9	87.5 (2)	C8—C7—O6	110.0 (4)
O11—Ni—O10	89.7 (2)	C8—C7—C6	134.6 (5)
C1—O1—Ni	126.0 (3)	C9—C8—C7	106.3 (5)
C5—O3—C2	105.5 (5)	C10—C9—C8	106.6 (5)
C10—O6—C7	105.5 (4)	C9—C10—O6	111.5 (5)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	H···*A*	*D*···*A*	*D*—H···*A*
O7	H71	O1	2.31 (5)	2.970 (5)	124 (4)
O7	H71	O2	1.62 (4)	2.575 (4)	168 (5)
O7	H72	O4	1.94 (5)	2.829 (4)	151 (4)
O8	H81	O1^{i}	1.78 (5)	2.702 (5)	156 (5)
O8	H82	O5^{ii}	2.31 (9)	2.912 (4)	120 (6)
O8	H82	O9^{i}	2.15 (6)	2.884 (4)	131 (6)
O9	H92	O5^{ii}	1.75 (6)	2.708 (5)	168 (5)
O9	H91	O5^{iii}	1.78 (2)	2.739 (4)	169 (4)
O10	H101	O7^{iv}	1.82 (4)	2.770 (4)	167 (4)
O10	H102	O4	1.76 (5)	2.707 (4)	164 (5)
O11	H111	O4^{iii}	1.67 (4)	2.620 (4)	166 (4)
O11	H112	O10^{i}	1.88 (4)	2.778 (5)	153 (5)

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

During the measurements the crystal was kept in a stream of cooled nitrogen. Preliminary Weissenberg photographs suggested space groups $C2$ or $C2/m$. C-bonded H atoms were placed in geometrically calculated positions (C—H = 1.08 Å). O-bonded H atoms were found from a difference Fourier synthesis and refined with constraints (O—H = 0.97 Å). The *y* coordinate of Ni was held constant to fix the origin. Refinement of the parameters for the inverted structure gave R = 0.0349 and wR = 0.0355. Data collection: Kuma KM-4 software. Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71745 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1070]

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Polyol Metal Complexes. VI.† Structure of Lithium Bis[methyl α-L-rhamnopyranosid-(2,3)-ato(2−)]cuprate(II) Tetrahydrate

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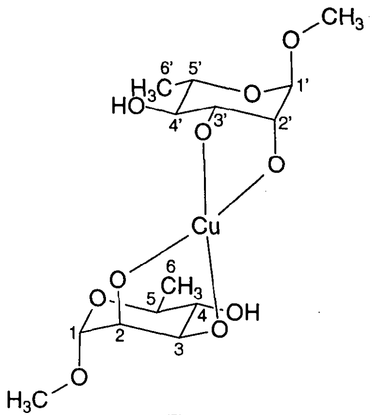
Abstract

Methyl α-L-rhamnopyranoside is deprotonated twice in the blue crystals of $Li_2[Cu(C_7H_{12}O_5)_2].4H_2O$. The sugar derivative acts as a chelate ligand in the homoleptic square-planar copper(II) complex. Furthermore, the alkoxide groups of the dianionic rhamnoside either bind to Li or act as acceptors in hydrogen bonds.

Comment

Only a few complexes of deprotonated carbohydrates with the later transition metals have been structurally characterized so far (Klaassen & Klüfers, 1993, and references therein; Fuchs, Habermann & Klüfers, 1993; Bhaduri, Sapre, Khwaja & Jones, 1992). We now report the crystal structure of the first coordination compound of a deprotonated rhamnose derivative.

Crystals of the title compound were grown from deep-blue aqueous solutions, which were prepared by the reaction of stoichiometric amounts of cupric nitrate, methyl α-L-rhamnopyranoside and excess lithium hydroxide. The X-ray structure determination reveals a square-planar homoleptic copper(II) complex, (I). The ligands are derived from the rhamnoside by deprotonation of the carbohydrate at O2 and O3, respectively. The resulting dianionic diolate ligand forms a five-membered chelate ring with the transition-metal ion. The planar geometry at the Cu atom is only slightly distorted [the dihedral angle between the planes Cu-O2-O3 and Cu-O2′-O3′ is 3.91 (13)°]. The conformational analysis of the copper chelate five-membered rings and of the pyranose rings is facilitated by the puckering parameters (Cremer & Pople, 1975): the conformation of the five-membered chelate ring Cu—O2′—C2′—C3′—O3′ [Q = 0.381 (3) Å, φ = 260.8 (3)°] is derived from a twist conformation $^4T_3$ with the metal ion as the pivot atom of the twist axis, distorted towards the E_3 conformation, *i.e.* an envelope conformation with C2′ as the out-of-plane atom (ideal φ values: 270° for $^4T_3$; 252° for E_3); the second five-membered ring Cu—O2—C2—C3—O3 [Q = 0.408 (3) Å, φ = 285.1 (3)°] has ^4E conformation (C3 as the out-of-plane atom, ideal φ = 288°). Each pyranose ring adopts an only slightly distorted $^1C_4$ conformation [for O5—C1—C2—C3—C4—C5—O5, Q = 0.557 (3) Å, θ = 173.0 (3)°, φ = 98 (2)°; for O5′—C1′—C2′—C3′—



(I)

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† Part V: Achternbosch & Klüfers (1994).