

## Hexaaquanickel(II) Dipotassium Tetrahydrogen Tetra-*o*-phthalate Tetrahydrate, $K_2[Ni(H_2O)_6][C_8H_5O_4]_4 \cdot 4H_2O$

BY MARINA BIAGINI CINGI, ANNA MARIA MANOTTI LANFREDI AND ANTONIO TIRIPICCHIO

*Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica  
 Diffattometrica del CNR, via M.D'Azeglio 85, 43100 Parma, Italy*

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**Abstract.**  $M_r = 977.56$ , monoclinic,  $P2_1/c$ ,  $a = 10.408(8)$ ,  $b = 6.864(4)$ ,  $c = 29.447(18)$  Å,  $\beta = 98.10(6)^\circ$ ,  $V = 2083(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.559$  g cm<sup>-3</sup>,  $\bar{\lambda} = 1.54178$  Å,  $\mu(Cu K\alpha) = 33.01$  cm<sup>-1</sup>,  $F(000) = 1012$ , room temperature. The structure has been solved by Patterson and Fourier methods and refined to  $R = 4.5\%$  for 3185 independent observed reflections. It consists of chains of hydrogen *o*-phthalate anions, joined in slices parallel to (001) with octahedral  $[Ni(H_2O)_6]^{2+}$  cations,  $K^+$  ions and water molecules interposing between these slices by hydrogen bonds and by  $K \cdots O$  interactions.

**Introduction.** Previous work (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1977a, 1978a,b,c,d, 1979, 1981) has pointed out the different bridging behaviour of the *o*-phthalate anion (pht), acting as a ligand to the  $Cu^{2+}$  cation, when different chemical species are present in the system. In an attempt to investigate how pht behaves when transition  $M^{2+}$  cations replace  $Cu^{2+}$ , pale-green crystals of the title compound were obtained, by slow evaporation at room temperature, from a solution (pH  $\sim 3$ ) of Ni and K carbonates in warm phthalic acid.

**Experimental.** Pale-green prismatic crystal,  $0.12 \times 0.15 \times 0.35$  mm, Siemens AED diffractometer, Ni-filtered  $Cu K\alpha$  radiation, 20 reflections for lattice-parameter measurements, 3951 independent reflections with  $2\theta < 140^\circ$  ( $-12 \leq h \leq 12$ ,  $0 \leq k \leq 8$ ,  $0 \leq l \leq 35$ ), 3185 with  $I > 2\sigma(I)$ , no significant intensity deterioration of standard reflection (911), Lp correction, absorption ignored; Patterson and Fourier methods for structure determination; full-matrix least-squares refinement (SHELX; Sheldrick, 1976); anisotropic thermal parameters for all the non-hydrogen atoms except for OW(5) and OW(6), occupancy sites for these are 0.67 and 0.33 respectively by refinement; H atoms, except for those of OW(5) and OW(6), located from  $\Delta F$  synthesis and refined isotropically;  $\sum_w |\Delta F|^2$  minimized with final  $R = 4.5\%$ ,  $wR = 4.7\%$ , unit weight in each stage of the refinement by analysing the variations of  $|\Delta F|$  as a function of  $|F_0|$ ;  $(\Delta/\sigma)_{max} = 0.1$ , final  $\Delta\rho$  excursions  $\leq |0.4| e \text{ \AA}^{-3}$ ; atomic scattering factors

from *International Tables for X-ray Crystallography* (1974); calculations performed on the CYBER76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna) with the financial support from the University of Parma.\*

\* Lists of structure factors, H-atom coordinates, hydrogen-bond data and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38821 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

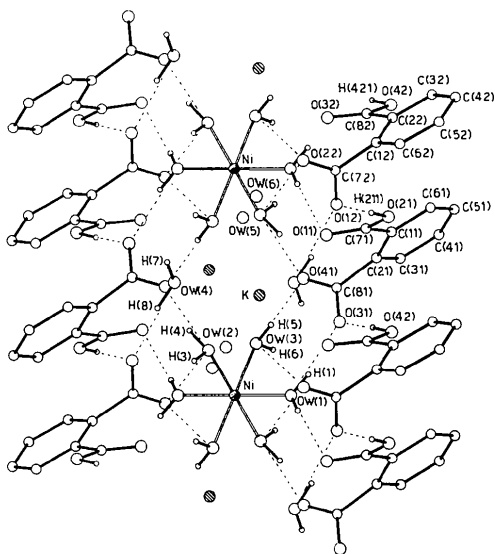
Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters for the non-hydrogen atoms with e.s.d.'s in parentheses

	$B_{eq} = \frac{2}{3}\pi^2 \text{ trace } \bar{U}$			
	$x$	$y$	$z$	$B_{eq}$ or $B(\text{\AA}^2)$
Ni	0	0	0	2.06 (5)
K	2921 (1)	4442 (2)	-261 (1)	4.68 (5)
OW(1)	814 (3)	-4 (5)	-589 (1)	4.03 (9)
OW(2)	1376 (3)	2023 (4)	271 (1)	2.85 (9)
OW(3)	-1196 (2)	2318 (4)	-227 (1)	2.64 (8)
OW(4)	3835 (7)	5004 (7)	626 (2)	13.24 (23)
OW(5)*	4673 (6)	7842 (11)	-91 (2)	6.39 (22)
OW(6)*	3729 (18)	8778 (28)	-232 (6)	9.71 (67)
O(11)	2444 (3)	7078 (6)	-959 (1)	4.53 (12)
O(21)	3164 (3)	7876 (5)	-1610 (1)	3.56 (10)
O(31)	890 (3)	3274 (5)	-1096 (1)	4.11 (9)
O(41)	-297 (3)	5171 (4)	-720 (1)	3.84 (10)
O(12)	5246 (3)	8434 (5)	-1067 (1)	4.09 (9)
O(22)	6773 (3)	10360 (5)	-721 (1)	4.27 (9)
O(32)	3821 (3)	12251 (6)	-975 (1)	4.69 (11)
O(42)	2572 (3)	12816 (5)	-1641 (1)	3.44 (9)
C(11)	934 (3)	7212 (6)	-1643 (1)	2.29 (9)
C(21)	-26 (3)	6085 (6)	-1481 (1)	2.31 (9)
C(31)	-1265 (4)	6060 (6)	-1731 (2)	3.16 (11)
C(41)	-1537 (4)	7083 (7)	-2136 (2)	3.79 (13)
C(51)	-593 (5)	8201 (7)	-2296 (1)	3.66 (11)
C(61)	639 (4)	8278 (6)	-2047 (1)	3.06 (12)
C(71)	2251 (4)	7357 (6)	-1372 (1)	2.53 (9)
C(81)	222 (3)	4777 (6)	-1066 (1)	2.54 (10)
C(12)	5874 (3)	11148 (5)	-1483 (1)	2.46 (9)
C(22)	4787 (3)	12251 (5)	-1656 (1)	2.33 (10)
C(32)	4758 (4)	13265 (6)	-2067 (1)	3.22 (10)
C(42)	5802 (5)	13154 (7)	-2312 (2)	4.20 (13)
C(52)	6877 (5)	12054 (7)	-2142 (2)	4.35 (14)
C(62)	6926 (4)	11085 (6)	-1731 (2)	3.57 (11)
C(72)	5962 (3)	9921 (6)	-1057 (1)	2.84 (10)
C(82)	3690 (3)	12424 (6)	-1386 (1)	2.77 (10)

\* Occupancy sites for OW(5) and OW(6) are 0.67 and 0.33 respectively.

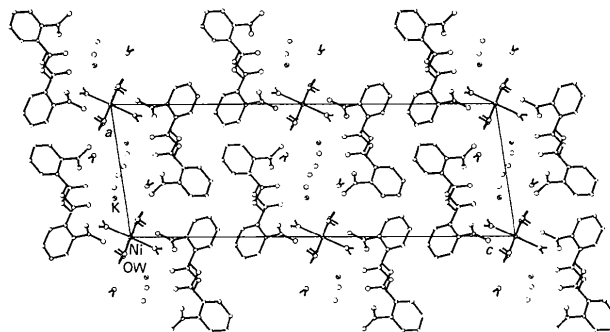
Table 2. Bond distances (Å) and angles (°)

In the hexaaquanickel cation			
Ni—OW(1)	2.035 (3)	Ni—OW(3)	2.072 (3)
Ni—OW(2)	2.072 (3)		
OW(1)—Ni—OW(2)	88.9 (2)	OW(2)—Ni—OW(3)	87.8 (1)
OW(1)—Ni—OW(3)	91.7 (2)		
In the hydrogen <i>o</i> -phthalate anions			
C(11)—C(21)	1.400 (5)	C(11)—C(71)	1.489 (5)
C(21)—C(31)	1.392 (5)	C(71)—O(11)	1.220 (4)
C(31)—C(41)	1.379 (8)	C(71)—O(21)	1.307 (5)
C(41)—C(51)	1.381 (7)	C(21)—C(81)	1.509 (5)
C(51)—C(61)	1.386 (6)	C(81)—O(31)	1.254 (5)
C(61)—C(11)	1.394 (5)	C(81)—O(41)	1.248 (5)
C(61)—C(11)—C(21)	120.0 (4)	O(21)—C(71)—C(11)	114.5 (3)
C(11)—C(21)—C(31)	118.6 (6)	O(11)—C(71)—C(11)	122.3 (4)
C(21)—C(31)—C(41)	120.9 (5)	O(11)—C(71)—O(21)	123.2 (4)
C(31)—C(41)—C(51)	120.6 (5)	C(81)—C(21)—C(11)	123.8 (4)
C(41)—C(51)—C(61)	119.4 (4)	C(81)—C(21)—C(31)	117.5 (4)
C(51)—C(61)—C(11)	120.5 (4)	O(31)—C(81)—C(21)	117.8 (4)
C(71)—C(11)—C(61)	119.9 (4)	O(41)—C(81)—C(21)	119.2 (4)
C(71)—C(11)—C(21)	120.1 (3)	O(31)—C(81)—O(41)	122.9 (4)
C(12)—C(22)	1.397 (5)	C(12)—C(72)	1.503 (5)
C(22)—C(32)	1.393 (5)	C(72)—C(12)	1.262 (5)
C(32)—C(42)	1.389 (7)	C(72)—O(22)	1.244 (4)
C(42)—C(52)	1.384 (7)	C(22)—C(82)	1.485 (5)
C(52)—C(62)	1.376 (8)	C(82)—O(32)	1.205 (4)
C(62)—C(12)	1.400 (6)	C(82)—O(42)	1.321 (4)
C(62)—C(12)—C(22)	118.7 (4)	O(22)—C(72)—C(12)	118.9 (4)
C(12)—C(22)—C(32)	120.3 (4)	O(12)—C(72)—C(12)	117.9 (4)
C(22)—C(32)—C(42)	120.1 (4)	O(12)—C(72)—O(22)	123.2 (4)
C(32)—C(42)—C(52)	119.6 (5)	C(82)—C(22)—C(12)	119.5 (3)
C(42)—C(52)—C(62)	120.7 (5)	C(82)—C(22)—C(32)	120.1 (4)
C(52)—C(62)—C(12)	120.6 (5)	O(32)—C(82)—C(22)	122.9 (4)
C(72)—C(12)—C(62)	117.3 (4)	O(42)—C(82)—C(22)	113.2 (3)
C(72)—C(12)—C(22)	124.0 (4)	O(32)—C(82)—O(42)	123.9 (4)
Around the K <sup>+</sup> cation			
K—O(11)	2.731 (4)	K—OW(2)	2.917 (4)
K—OW(4)	2.679 (7)	K—OW(5)	2.961 (7)
K—O(32 <sup>1</sup> )	2.849 (4)	K—OW(6)	3.091 (19)
K—O(31)	3.113 (4)	K—OW(5 <sup>11</sup> )	3.012 (7)

Symmetry code: (i)  $x, -1 + y, z$ ; (ii)  $1 - x, 1 - y, -z$ .Fig. 1. View along *a* of a portion of the structure with the atomic numbering scheme.

**Discussion.** Table 1 shows the atomic parameters, Table 2 the bond distances and angles. The crystal structure, depicted in Fig. 1, consists of octahedral hexaaquanickel cations, K<sup>+</sup> ions, hydrogen *o*-phthalate anions (Hpht) and water molecules; the Hpht ions are connected (as is usually found in the structure of hydrogen *o*-phthalate derivatives) in chains, running along *b*, by short intermolecular hydrogen bonds involving the hydroxyl moiety of the carboxylic group of a Hpht ion and an O atom of the carboxylate group from an adjacent Hpht anion. The Ni—OH<sub>2</sub> distances [2.035 (3)—2.072 (3) Å] (the Ni ions occupying inversion centres) show the same pattern as in other previously recorded Ni—O bond lengths, in particular in nickel dihydrogen diphthalate hexahydrate (Adiwidjaja & Küppers, 1976). The K<sup>+</sup> ions are surrounded by O atoms [at distances in the range 2.679 (7)—3.113 (4) Å] from Hpht ions of a chain and from Ni-bonded and free water molecules [the free OW(5) and OW(6) water molecules being in statistical positions]. In both independent Hpht anions the C—O distances of the carboxylate group are similar, with the C—C—O angles involved almost equivalent; the carboxylic group, instead, shows a significant difference in the C—O distances (the longer involving the protonated oxygen) in both Hpht anions, with the C—C—OH angle significantly narrower than the C—C=O angle.

Also the conformations of the two independent Hpht anions are very similar. In each Hpht both carboxylic and carboxylate groups are rotated around their C—C bonds on the opposite sides with respect to the benzene plane by angles which are narrower for the carboxylic groups (23.8 and 26.5° respectively) with respect to those of the carboxylate groups (70.6 and 68.6°). This situation is generally found in the structure in which the Hpht anions are connected in infinite chains by intermolecular hydrogen bonds (Bats, Schuckmann & Fuess, 1978; Adiwidjaja & Küppers, 1976; Adiwidjaja, Rossmannith & Küppers, 1978). A different situation has been found for the Hpht anion in the structure of diaquabis(hydrogen *o*-phthalato)copper(II) (Biagini

Fig. 2. Projection of the structure along *b*.

Cingi, Guastini, Musatti & Nardelli, 1969) and tris-(thiourea)copper(I) hydrogen *o*-phthalate (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1977b) where the slight rotation of the carboxylic and carboxylate groups on opposite sides by nearly the same angles is determined by a strong intramolecular hydrogen bond.

The chains of the Hpht anion, held together by van der Waals contacts, are arranged through the screw axes at  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$  in slices parallel to (001) (Fig. 2). K<sup>+</sup> ions, octahedral hexaaquanickel cations and water molecules interpose between these slices linked through K<sup>+</sup>···O interactions and hydrogen bonds that the O atoms of Hpht ions, from different slices, form with the free and Ni-coordinated water molecules.

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## Calcium Naphthionate Octahydrate, Ca<sup>2+</sup>·2C<sub>10</sub>H<sub>8</sub>NO<sub>3</sub>S<sup>-</sup>·8H<sub>2</sub>O\*

BY C. J. BROWN, M. EHRENBURG AND H. R. YADAV

*Department of Metallurgy and Materials Engineering, City of London Polytechnic, Central House, Whitechapel High Street, London E1 7PF, England*

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**Abstract.**  $M_r = 628.7$ , monoclinic,  $P2_1/n$ ,  $a = 23.605$  (16),  $b = 11.931$  (9),  $c = 9.708$  (10) Å,  $\beta = 94.0$  (1)°,  $V = 2727.42$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.528$  (1),  $D_x = 1.53$  Mg m<sup>-3</sup>,  $Cu K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 3.9$  mm<sup>-1</sup>,  $F(000) = 1320$ ,  $R = 0.029$  for 4467 observed reflexions [ $I > 3\sigma(I)$ ]. The Ca<sup>2+</sup> ion is seven coordinated to water oxygens which are hydrogen bonded to sulphonate oxygens and amino nitrogens. All the bond lengths and inter-bond angles have standard values and there are no geometric peculiarities.

**Introduction.** The title compound is the neutral calcium salt of naphthionic acid. The crystal structure determination was undertaken because of the similarity of the unit-cell dimensions to those of the sodium salt (Corbridge, Brown & Wallwork, 1966), *i.e.*  $a = 11.613$ ,  $b = 12.053$ ,  $c = 10.045$  Å,  $\beta = 98.8$ °,  $P2_1/c$ . Comparison

\* Calcium 4-amino-1-naphthalenesulphonate octahydrate. (Note that the atomic numbering used throughout corresponds to the alternative description 1-amino-4-naphthalenesulphonate octahydrate.)

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of one unit cell of the Ca salt with two of the Na salt shows that for every two Na<sup>+</sup> ions there is only one Ca<sup>2+</sup> ion, and there was some speculation concerning the environment of the supposedly vacant site. It was thought that the situation might be similar to that found in the structures of lithium and magnesium perchlorates (West, 1934, 1935).

**Experimental.** Crystals by slow evaporation of a solution of naphthionic acid in 1% calcium hydroxide, equi-dimensional crystals *ca* 0.3 mm, density by flotation in a mixture of organic liquids; accurate lattice parameters by least-squares analysis of the  $\alpha_1\alpha_2$  separations of 75 reflexions taken about **b** and **c** in a 57.3 mm radius camera;  $h0l$  absent for  $(h+l)$  odd,  $0k0$  absent for  $k$  odd; intensities by visual estimation,  $h0l-h, 12, l$  and  $hk0$  on Weissenberg photographs using multiple-film packs, index range  $h$  0–30,  $k$  0–14,  $l$   $\pm$ 12; no absorption correction, empirical modifications for secondary extinction during refinement for a small number of very intense reflexions; structure solved by