

**Discussion.** Tables 1 and 4 illustrate the close similarity between  $\text{UO}_2\text{SeO}_3$  and  $\text{UO}_2\text{TeO}_3$  [O(3) in Table 1 corresponding to O(3) and O(4) in Table 4]. For the comparison the  $z$  parameters of Table 1 have to be changed to  $0.250 + z/2$  because of the shift of origin and the doubling of  $c$  in the tellurite.

Although the two structures are topologically identical the two compounds are not isostructural. In  $\text{UO}_2\text{SeO}_3$  the selenite ion has its usual trigonal-pyramidal shape; the U coordination is hexagonal bipyramidal (regarding the O atoms at 2.64 Å as part of the coordination polyhedron). This coordination is unusual for  $\text{U}^{\text{VI}}$ . In the tellurite the  $\text{Te}^{\text{IV}}$  coordination is close to the normal trigonal bipyramid with an empty site in the base plane (Zemann, 1971). As in  $\alpha\text{-TeO}_2$  (Lindqvist, 1968) the tellurite ion has a twofold axis. In the tellurite the U is coordinated by a pentagonal-bipyramidal arrangement of O atoms, which is rather more distorted than usual, apparently caused by O(1) at 3.45 Å.

$\text{UO}_2\text{SeO}_3$  is unstable in air and towards moisture, while  $\text{UO}_2\text{TeO}_3$  occurs as a mineral. Both structures exhibit a large number of strong bonds in the  $yz$  layers, but the coherence in the  $x$  direction is small: two Se—O bonds of 3.06 Å per Se atom in the selenite and two Te—O bonds of 3.11 and two of 3.18 Å per Te atom in the tellurite. No other bonds exist up to the 3.5 Å limit calculated. If the valence of these bonds is calculated

from the parameters given by Brown & Wu (1976) we find a value of 0.12 for the selenite and 0.12 and 0.11 for the tellurite bonds. These values indicate that the interlayer bond strength in the tellurite is twice that in the selenite. From the structures no other plausible explanation is found for the difference in stability between  $\text{UO}_2\text{SeO}_3$  and  $\text{UO}_2\text{TeO}_3$ .

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### Tetraaquabis(*m*-chlorobenzoato)nickel(II)

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**Abstract.**  $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{O}_8\text{Ni}$ ,  $M_r = 441.89$ , triclinic,  $P\bar{1}$ ,  $a = 6.273$  (1),  $b = 10.021$  (1),  $c = 13.696$  (2) Å,  $\alpha = 90.14$  (1),  $\beta = 95.74$  (1),  $\gamma = 93.55$  (1)°,  $Z = 2$ ,  $D_c = 1.72$ ,  $D_m = 1.71$  (2)  $\text{g cm}^{-3}$ ;  $R = 0.048$  for 2466 observed reflections. In this molecular compound the Ni atom is coordinated to O atoms in a pseudo-octahedral arrangement involving *trans* monodentate carboxylate anions.

**Introduction.** Initial precession photographs of a prismatic green crystal (0.3 mm) indicated a triclinic

unit cell which structure analysis later showed to be  $P\bar{1}$ . The crystal was transferred to a Picker FACS-I fully automated diffractometer ( $b^*$  axis coincident with  $\varphi$  axis) and lattice constants were determined from 26 intense reflections by a least-squares fit to carefully measured  $\pm 2\theta$  values ( $60 < 2\theta < 78^\circ$ ) for the  $\text{Cu } K\alpha_1 - K\alpha_2$  doublet [ $\lambda(\text{Cu } K\alpha_1) = 1.54050$  Å;  $\lambda(\text{Cu } K\alpha_2) = 1.54433$  Å]. Intensity data were collected to a  $2\theta_{\text{max}}$  of  $125^\circ$  with Ni-filtered  $\text{Cu } K\alpha$  radiation (as the only available source) using a fixed  $\theta/2\theta$  scan rate of  $2^\circ \text{ min}^{-1}$ . A variable scan width of  $2.3^\circ + 0.4^\circ \tan \theta$  with

10 s background measurements at scale extremities was used to determine intensities of 2725 independent reflections. Three periodically measured reference reflections showed a random variation of  $\pm 2\%$  and no systematic decay. Reflection intensities were corrected for absorption as a function of their  $\varphi$  angle settings relative to a  $\varphi$  scan measurement of the 002 reflection at  $\chi = 90^\circ$ ; the ratio of intensity extremes for the 002 reflection was 1:0.58 as compared with 1:0.56 calculated for the crystal shape and  $\mu = 46.6 \text{ cm}^{-1}$ . Correction for Lorentz and polarization effects was applied in the usual manner.

The structure was solved by a combination of heavy-atom and Fourier synthesis methods. Structure refinement utilized full-matrix least-squares calculations which minimize the function  $\sum w(|F_o| - |F_c|)^2$  with weights of  $1/\sigma^2$  where  $\sigma^2(F_o) = (F_o/2I_n)^2[I_s + (t_s/t_b)^2I_b + (0.02I_n)^2]$ ;  $I_s$ ,  $I_b$  and  $I_n$  are scan, background and net

Table 1. Final positional parameters

Estimated standard deviations are in parentheses.

	x	y	z
Ni	-0.02796 (9)	0.25637 (6)	0.01571 (4)
Cl(1)	0.1406 (2)	-0.2115 (1)	0.4063 (1)
Cl(2)	-0.1679 (2)	0.6931 (1)	-0.3938 (1)
O(1)	0.2220 (4)	0.4002 (3)	0.0134 (2)
O(2)	0.1128 (5)	0.1438 (3)	-0.0831 (2)
O(3)	-0.2709 (4)	0.1066 (3)	0.0158 (2)
O(4)	-0.1634 (5)	0.3771 (3)	0.1163 (2)
O(5)	0.1168 (4)	0.1596 (2)	0.1334 (2)
O(6)	0.4528 (4)	0.2360 (3)	0.1211 (2)
O(7)	-0.1866 (4)	0.3554 (2)	-0.0986 (2)
O(8)	-0.4778 (4)	0.2177 (3)	-0.1335 (2)
C(1)	0.3135 (6)	0.1635 (3)	0.1599 (3)
C(2)	0.3904 (6)	0.0761 (4)	0.2439 (3)
C(3)	0.2476 (7)	-0.0161 (4)	0.2814 (3)
C(4)	0.3204 (7)	-0.0969 (4)	0.3580 (3)
C(5)	0.5314 (8)	-0.0877 (5)	0.3966 (3)
C(6)	0.6722 (7)	0.0047 (5)	0.3594 (3)
C(7)	0.6040 (7)	0.0860 (4)	0.2826 (3)
C(8)	-0.3623 (6)	0.3199 (4)	-0.1488 (3)
C(9)	-0.4322 (6)	0.4081 (4)	-0.2332 (3)
C(10)	-0.2876 (7)	0.5025 (4)	-0.2679 (3)
C(11)	-0.3534 (7)	0.5803 (4)	-0.3470 (3)
C(12)	-0.5609 (8)	0.5701 (5)	-0.3896 (3)
C(13)	-0.7051 (8)	0.4770 (5)	-0.3544 (4)
C(14)	-0.6417 (7)	0.3957 (4)	-0.2766 (3)
H(O1)	0.212 (7)	0.459 (4)	0.051 (3)
H'(O1)	0.323 (8)	0.365 (5)	0.046 (4)
H(O2)	0.216 (8)	0.173 (5)	-0.102 (4)
H'(O2)	0.132 (7)	0.077 (5)	-0.061 (4)
H(O3)	-0.338 (7)	0.124 (4)	-0.041 (3)
H'(O3)	-0.350 (9)	0.131 (5)	0.052 (4)
H(O4)	-0.279 (8)	0.347 (5)	0.135 (4)
H'(O4)	-0.184 (8)	0.441 (5)	0.084 (4)
H(C3)	0.109 (6)	-0.025 (3)	0.258 (3)
H(C5)	0.578 (7)	-0.140 (5)	0.451 (4)
H(C6)	0.823 (7)	0.021 (5)	0.386 (4)
H(C7)	0.693 (6)	0.151 (4)	0.253 (3)
H(C10)	-0.148 (6)	0.510 (4)	-0.244 (3)
H(C12)	-0.607 (8)	0.622 (5)	-0.442 (4)
H(C13)	-0.853 (7)	0.464 (5)	-0.389 (4)
H(C14)	-0.733 (6)	0.335 (4)	-0.251 (3)

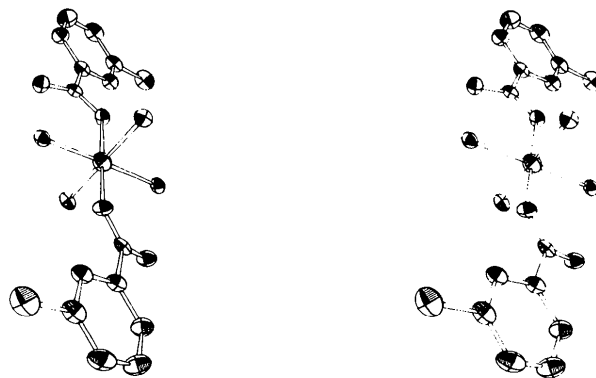
Table 2. Angles about nickel (*e.s.d.* = 0.1°)

O(2)-Ni-O(1)	89.3°	O(5)-Ni-O(3)	85.7°
O(3) O(1)	177.7	O(5) O(4)	87.8
O(3) O(2)	88.5	O(7) O(1)	87.8
O(4) O(1)	88.7	O(7) O(2)	90.0
O(4) O(2)	178.0	O(7) O(3)	92.9
O(4) O(3)	93.5	O(7) O(4)	89.7
O(5) O(1)	93.6	O(7) O(5)	177.1
O(5) O(2)	92.5		

intensities, and  $t_s$  and  $t_b$  are scan and background times. Scattering factors for nonhydrogen atoms were taken from tabulations of Cromer & Waber (1965), and from Stewart, Davidson & Simpson (1965) for the H atoms. Anomalous-dispersion corrections for both real and imaginary terms were applied to Ni and Cl structure factors (Cromer & Liberman, 1970). Nonhydrogen atoms were readily located in sequential Fourier syntheses and anisotropic refinement on these atomic positions converged with  $R = 0.063$ . All H atoms were found in a difference Fourier map and included in the refinement as isotropic atoms. A final two cycles of refinement on 2466 reflections with  $|F_o| > 3\sigma(F_o)$  resulted in residuals  $R = 0.048$  and  $R_w = 0.054$ , where  $R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$ ;  $R = 0.052$  for all 2725 measured reflections. Final positional parameters are given in Table 1, a drawing of the molecule is shown in Fig. 1, bond lengths and selected angles are shown in Fig. 2, and the remaining intramolecular angles are listed in Table 2.\*

**Discussion.** Coordination of transition metals to carboxylate anions is a broad area of chemical interest which has received much attention, especially in terms

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33228 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 1. A stereoview of the  $\text{Ni}(m\text{-Cl-BzO})_2 \cdot 4\text{H}_2\text{O}$  molecule (ORTEP, Johnson, 1965).

of correlating spectral character with structural features (Oldham, 1968). Our particular interest in this field has centered on the benzoate anion and its compounds with first-row transition metals (Pavkovic, 1971). In this regard we have undertaken the synthesis and spectral characterization of several substituted-benzoato metal complexes and have recently reported the preparation and properties of a series of hydrated Ni<sup>II</sup> complexes containing ring-substituted halobenzoate anions (Wilhelm & Pavkovic, 1975). These compounds are unique because their degree of hydration is directly related to the position of the halo substituent and is quite independent of the particular halogen atom present. They may all be represented by the general formula Ni(*X*-BzO)<sub>2</sub>·YH<sub>2</sub>O, but *Y* is 1 for *o*-*X*, 4 for *m*-*X*, and 3 for *p*-*X*. This singular dependence on ring-position poses questions about the structural role of the halogen substituent which prompted the current crystallographic structure determination for a member of the *meta*-substituted series.

The crystal structure of the title compound is composed of discrete molecules in which the Ni atom is bonded in a pseudo-octahedral manner to four O atoms from water molecules and two from *trans*-monodentate benzoate anions. Five of the Ni-O bond distances average 2.06 (1) Å, as found in nickel formate dihydrate (Krogmann & Mattes, 1963), and

nickel acetate tetrahydrate (Cramer, Van Doorne & Dubois, 1975, and references therein), but the sixth separation [Ni-O(4)] is significantly longer at 2.106 (3) Å. However, even this is within the range of values reported for Ni-O(water) bonding distances, as in the stilbenediamine complex (Nyburg & Wood, 1964). Nevertheless, the cause for the elongation here is unclear since remaining contacts to O(4) are neither as numerous nor as short as those to other O atoms in the structure. Angles that coordinated atoms subtend at the Ni atom are all near 90 or 180° without notable exception (Table 2).

The two phenyl rings per molecule, which are effectively coplanar, are set at angles of 14.6 and 12.8° to the coordination plane containing Ni and O(1), O(3), O(5) and O(7). The dihedral angles between carboxylate groups and their bonded phenyl rings are 7.2 and 16.5° respectively. These two groups are also non-planar in metal-benzoate complexes of Cu (Koizumi, Osaki & Watanabe, 1963) and Re (Bratton & Cotton, 1969), and in nickel thiobenzoate with dihedral angles of 7 to 38° (Melson, Green & Bryan, 1970). In the first case the plane of the Ni atom and the carboxylate group atoms, O(5) and O(6), crosses the coordination plane at 22.3° and carbonyl atom O(6) is 0.78 Å removed from the plane. A similar atomic arrangement is found in nickel acetate tetrahydrate where corresponding values are 23.0° and 0.85 Å; carboxylate groups in nickel formate dihydrate are bridging and not comparable. However, the second carboxylate group is almost coplanar with the coordination plane with a dihedral angle of 4.5° for the O(7)-Ni-O(8) plane of atoms, and O(8) located 0.11 Å from the coordination plane. This difference in environment of carbonyl O

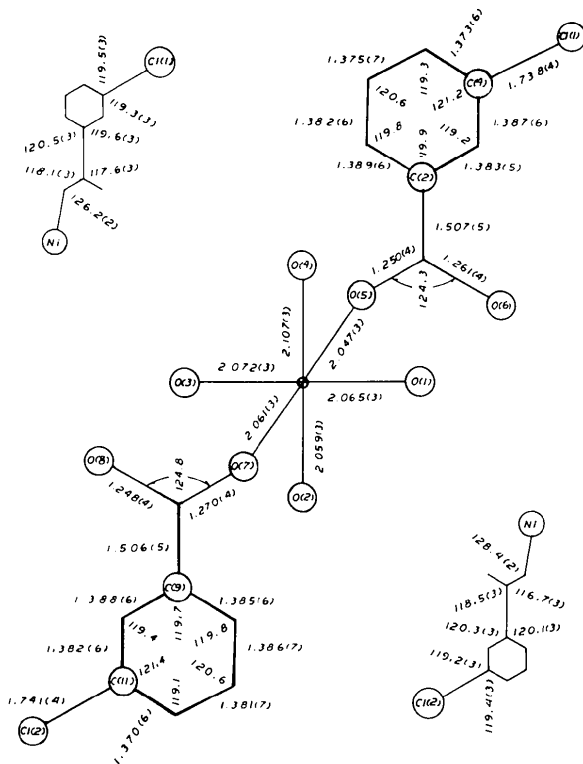


Fig. 2. A schematic representation of the Ni(*m*-Cl-BzO)<sub>2</sub>·4H<sub>2</sub>O molecule with bond distances Å and angles (°) indicated.

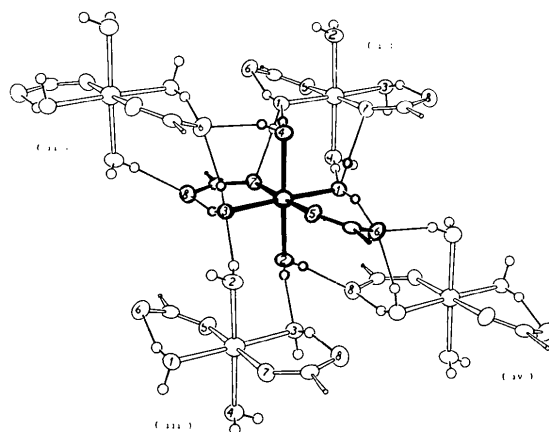


Fig. 3. An ORTEP diagram showing one Ni(*m*-Cl-BzO)<sub>2</sub>·4H<sub>2</sub>O molecule and all of its hydrogen bonds to/from neighboring molecules (O atoms are numbered and *m*-Cl-phenyl rings have been omitted for clarity). The molecule described by the table of fractional coordinates has shaded bonds, and neighboring molecules are the equivalent positions (i)···(iv) described in the text.

atoms results in differences in their hydrogen-bonding capabilities (see below). Surprisingly, both non-coordinated O atoms are situated on the same side of the coordination plane, opposite the elongated Ni—O(4) bond. According to the precision of our data, C(1)—O(5) and C(1)—O(6) bond distances are equivalent although C—O(uncoordinated) bond lengths are expected to be shorter, as found in nickel acetate tetrahydrate and copper hippurate (Brown & Trefonas, 1973). Bonding distances and angles within both carboxylate groups and phenyl rings are similar to values reported in related structures (*International Tables for X-ray Crystallography*, 1968). The complete molecule is roughly centrosymmetric.

The Cl atoms are well isolated in this structure and nearest non-bonded contacts are between Cl(2) and a neighboring-ring atom C(2<sup>i</sup>) at 3.5 Å and O(5<sup>i</sup>) at 3.8 Å [equivalent positions for neighboring molecules are (i) =  $\bar{x}, 1 - y, \bar{z}$ ; (ii) =  $-1 + x, y, z$ ; (iii) =  $\bar{x}, y, \bar{z}$ ; (iv) =  $1 + x, y, z$ ]. This lack of any direct interaction between Ni and Cl atoms would account for the higher degree of hydration in these *meta*-substituted halobenzoato complexes as a means of satisfying the coordination requirements of the Ni atom.

All water molecules participate in the following hydrogen-bonding network (as illustrated in Fig. 3). O(1) and O(3) are four-coordinate with single bonds to Ni and three hydrogen bonds (donor, donor, acceptor) to [O(6), O(7<sup>i</sup>), O(4<sup>i</sup>)] and [O(8), O(6<sup>ii</sup>), O(2<sup>iii</sup>)] respectively; O(2) and O(4) are three-coordinate and hydrogen bonded (donor, donor) to [O(3<sup>iii</sup>), O(8<sup>iv</sup>)] and [O(1<sup>i</sup>), O(6<sup>ii</sup>)] respectively. Average bond parameters in the network are: bonded O—H distance, 0.80 (5) Å; hydrogen-bonded O...O contact, 2.7 (1) Å; and O...H—O angle, 162 (5)°. The eight hydrogen bonds are not equitably distributed since carboxylate atoms O(5) through O(8) participate in zero, three, one and two hydrogen bonds respectively, as shown in Fig. 3.

This represents a significant departure from the hydrogen-bonding scheme in the comparable nickel acetate tetrahydrate, and is due to the unequal disposition of the carboxylate groups (see above). The entire network operates in the *ab* plane and results in marked cleavage properties for the macroscopic crystal.

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### Dichloro(1-2:5-6- $\eta$ -cyclooctatetraene)palladium(II)

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**Abstract.** C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>Pd, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 11.608 (2), *b* = 9.637 (2), *c* = 7.844 (2) Å,  $\beta$  = 98.45 (5)° at 22°C, *Z* = 4, *D<sub>m</sub>* = 2.13 (2), *D<sub>x</sub>* = 2.15 g cm<sup>-3</sup>, FW 281.46,  $\Sigma|AF|/\Sigma F_o$  = 0.0189 from 1508 reflections.

The complex is a monomer with the two Cl atoms and the centers of the 1–2 and 5–6 double bonds of the cyclooctatetraene ligand lying in a plane with approximately 90° bond angles. Pd—C = 2.203 (2), 2.211 (3),