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Diaquabis[μ-(R,R)-tartrato-κ^4O^1,O^2:O^3,O^4]dinickel(II) trihydrate

Sandra Scherb, Christian Näther and Wolfgang Bensch*

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 40, D-24089 Kiel, Germany
Correspondence e-mail: wbensch@ac.uni-kiel.de

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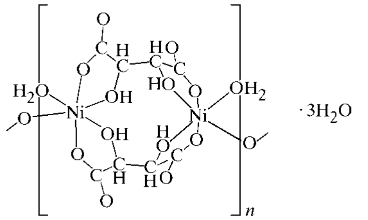
In the crystal structure of the title compound, $[Ni_2(C_4H_4O_6)_2(H_2O)_2]\cdot 3H_2O$, two nickel cations, two tartrate anions and two water molecules form the dimeric complex. Each nickel cation is in a distorted octahedral environment composed of four O atoms of two crystallographically independent tartrate anions, one water molecule and one O atom of a symmetry-equivalent tartrate anion. The asymmetric unit contains three additional water molecules which are connected *via* hydrogen bonding.

Comment

In 1984, Bostelaar *et al.* (1984) reported the crystal structure of diaquabis[(R,R)-tartrato-O^1,O^2:O^3,O^4]dinickel(II) trihydrate. The orthorhombic unit cell had a = 7.805 (3) Å, b = 11.068 (4) Å and c = 8.974 (8) Å, with Z = 2. From the systematic extinctions, chiral space group $P2_12_12$ was selected. In the crystal structure, some disordering of the incorporated water molecules was observed and very short intermolecular O···O distances occurred. In addition, some atoms of the tartrate anions showed unusual anisotropic displacement parameters.



(I)

During our investigations on the synthesis of new nickel thioantimonates under solvothermal conditions, we obtained crystals of the same composition as Bostelaar *et al.* (1984). In contrast to the previously reported structure, we found an orthorhombic unit cell with a doubled c axis. The systematic extinctions are in accordance with chiral space group $P2_12_12_1$. Without the doubled c axis, the systematic extinctions lead to space group $P2_12_12$. We note that the doubled c axis is observed at 295 and 150 K, thus excluding the possibility that the doubling is caused by a low-temperature phase transition.

The asymmetric unit of the title compound, (I), contains two crystallographically independent nickel cations and tartrate anions, as well as five crystallographically independent molecules of water, all of which are located in general positions (Fig. 1). Each Ni^{2+} cation is connected to two halves of two different tartate dianions through chelation by the alcohol and carboxylate groups, forming dimeric [(R,R)-tartrato-O^1,O^2:O^3,O^4]dinickel(II) complexes. The remaining two coordination sites of the Ni^{2+} cation are occupied by one water molecule and one O atom of a non-chelating carboxylate group from a symmetry-equivalent dimeric complex. As expected, the Ni—O distances to the chelating carboxylate O atoms [2.007 (2)–2.013 (2) Å] are significantly shorter than those to the hydroxyl O atoms [2.066 (2)–2.100 (2) Å]. The Ni—O distances to O atoms of the water molecules range from 2.031 (2) to 2.033 (2) Å and the distances to the non-chelating carboxylate O atoms are between 2.043 (2) and 2.046 (2) Å. The coordination polyhedron around the two crystallographically independent Ni^{2+} cations can be described as a distorted octahedron. The dimers are additionally connected by O—H···O hydrogen bonding between the H atoms of the water molecules, which are coordinated to the Ni^{2+} cations, and the carboxylate O atoms of symmetry-equivalent dimers, which act as acceptors. For these contacts, the shortest intermolecular O···H distances are 1.82 [O···O 2.638 (2) Å] and 1.82 Å [O···O 2.590 (2) Å], and the corresponding O—H···O angles are 178 and 157°. The three additional crystallographically independent water molecules connect the dimers *via* O—H···O hydrogen bonding. These water molecules act as acceptors for the H atoms of the tartrate hydroxyl groups and as donors for hydrogen bonds to the carboxylate O atoms and to other water molecules. The distances and angles indicate strong hydrogen bonds (Table 2).

Concerning the geometry of the tartrate anions in space group $P2_12_12$, the dimeric complexes are located around a twofold axis and the tartrate dianions must therefore be equivalent for symmetry reasons. A detailed analysis of the conformation of both crystallographically independent

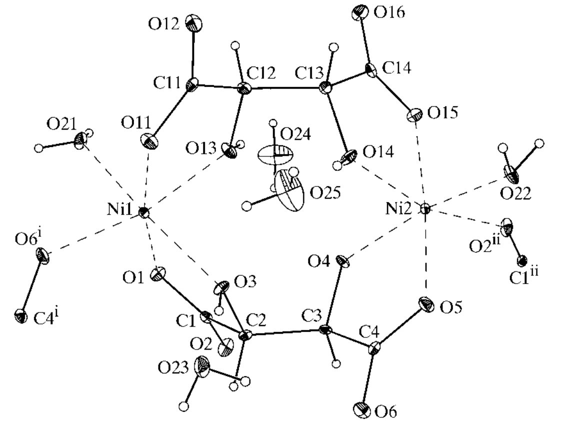


Figure 1
The crystal structure of (I) with the atom labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

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tartrate molecules in the title compound shows small but significant differences in their geometry.

Experimental

The title compound was prepared by the reaction of powdered nickel (1 mmol) with 1,3-phenylenediamine (1 mmol) in a colloidal solution of Sb_2S_3 (1%, 10 ml) which was stabilized with potassium antimony tartrate. The mixture was heated in a Teflon-lined steel autocalve at 413 K for 6 d. After cooling, the product as green crystals was filtered off and washed with water.

Crystal data

$[Ni_2(C_4H_4O_6)_2(H_2O)_2]\cdot 3H_2O$
$M_r = 503.64$
Orthorhombic, $P2_12_12_1$
$a = 7.8072$ (5) Å
$b = 11.0636$ (8) Å
$c = 17.9361$ (9) Å
$V = 1549.24$ (17) Å^3
$Z = 4$
$D_x = 2.159$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
$\theta = 3$–28°
$\mu = 2.53$ mm^{-1}
$T = 150$ (2) K
Block, green
0.3 × 0.2 × 0.2 mm

Data collection

Stoe Imaging Plate Diffraction System
φ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
$T_{\min} = 0.605$, $T_{\max} = 0.735$
22 323 measured reflections

3665 independent reflections
3602 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 28.1°$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.063$
$S = 1.06$
3665 reflections
245 parameters
constrained
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.7939P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.80$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0083 (7)
Absolute structure: Flack (1983)
Flack parameter = 0.002 (9), 1576 Friedel equivalents

Hydroxy H atoms were located from a difference map but were refined as rigid groups with idealized O—H bond lengths of 0.82 Å. H atoms on C atoms were positioned with idealized geometry and refined using a riding model. All H atoms were refined using fixed isotropic displacement parameters [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for methylene H atoms or $1.5U_{\rm eq}({\rm O_{OH}})$]. The absolute structure was determined using the Flack x parameter and is in agreement with the selected setting. In addition, inversion of the structure leads to significantly poorer reliability factors [$R1$ for all reflections with $F_o > 4\sigma(F_o) = 0.045$; $wR2$ for all reflections = 0.121]. The structure contains an additional pseudosymmetry element which is a translation in the direction of the c axis by 0.5.

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

Table 1
Selected geometric parameters (Å, °).

Ni1—O11	2.0091 (15)	Ni2—O15	2.0132 (15)
Ni1—O1	2.0121 (15)	Ni2—O22	2.0308 (15)
Ni1—O21	2.0328 (15)	Ni2—O2^{ii}	2.0430 (15)
Ni1—O6^{i}	2.0456 (15)	Ni2—O14	2.0688 (15)
Ni1—O13	2.0655 (15)	Ni2—O4	2.0914 (14)
Ni1—O3	2.0995 (15)	O2—Ni2^{iii}	2.0430 (15)
Ni2—O5	2.0066 (16)		
O11—Ni1—O1	169.38 (6)	O5—Ni2—O15	173.25 (6)
O11—Ni1—O21	87.68 (6)	O5—Ni2—O22	86.76 (6)
O1—Ni1—O21	97.08 (6)	O15—Ni2—O22	94.06 (7)
O11—Ni1—O6^{i}	94.70 (6)	O5—Ni2—O2^{ii}	99.26 (7)
O1—Ni1—O6^{i}	95.41 (6)	O15—Ni2—O2^{ii}	87.49 (6)
O21—Ni1—O6^{i}	81.08 (6)	O22—Ni2—O2^{ii}	81.38 (6)
O11—Ni1—O13	79.78 (6)	O5—Ni2—O14	94.21 (6)
O1—Ni1—O13	90.93 (6)	O15—Ni2—O14	79.10 (6)
O21—Ni1—O13	87.26 (6)	O22—Ni2—O14	89.82 (6)
O6^{i}—Ni1—O13	167.32 (7)	O2^{ii}—Ni2—O14	163.42 (6)
O11—Ni1—O3	94.67 (6)	O5—Ni2—O4	79.58 (6)
O1—Ni1—O3	79.66 (6)	O15—Ni2—O4	99.32 (6)
O21—Ni1—O3	173.76 (6)	O22—Ni2—O4	166.24 (6)
O6^{i}—Ni1—O3	104.45 (6)	O2^{ii}—Ni2—O4	102.32 (6)
O13—Ni1—O3	87.47 (6)	O14—Ni2—O4	89.55 (6)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$A\cdots$O23	0.82	1.99	2.797 (2)	168
O4—H4$A\cdots$O23^{i}	0.82	1.96	2.776 (2)	173
O13—H13$A\cdots$O24	0.82	1.87	2.655 (2)	160
O14—H14$A\cdots$O25	0.82	1.85	2.640 (2)	162
O21—H21$A\cdots$O16^{ii}	0.82	2.03	2.823 (2)	162
O21—H21$B\cdots$O12^{iii}	0.82	1.82	2.638 (2)	178
O22—H22$A\cdots$O12^{iv}	0.82	1.96	2.679 (2)	145
O22—H22$B\cdots$O16^{v}	0.82	1.82	2.590 (2)	157
O23—H23$A\cdots$O22^{vi}	0.82	2.00	2.811 (2)	170
O23—H23$B\cdots$O1^{vii}	0.82	1.91	2.718 (2)	167
O24—H24$A\cdots$O11^{i}	0.82	2.16	2.820 (2)	137
O24—H24$B\cdots$O5^{viii}	0.82	2.60	3.382 (3)	160
O25—H25$A\cdots$O15^{ix}	0.82	2.06	2.792 (2)	148
O25—H25$B\cdots$O24^{ix}	0.82	2.59	3.299 (3)	146

Symmetry codes: (i) $x - 1, y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (iv) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (v) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (vi) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vii) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ix) $1 + x, y, z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1097). Services for accessing these data are described at the back of the journal.

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