

A novel Na–O–Ni–O–Ni bridging complex of Cl-HXTA, where Cl-HXTA is 2,6-bis[[bis(carboxylatomethyl)-amino]methyl]-4-chlorophenolate

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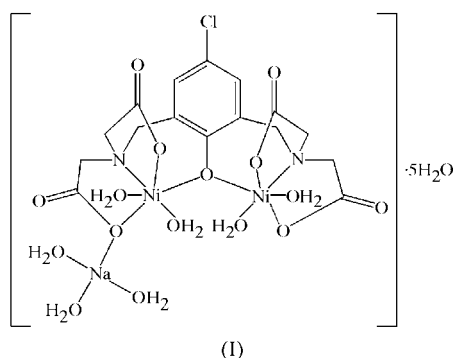
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In the structure of the title compound, heptaqua- $1\kappa^3O,2\kappa^2O,3\kappa^2O-(\mu_3-2,6$ -bis[[bis(carboxylatomethyl)amino]methyl]-4-chlorophenolato- $1\kappa O;2\kappa^4O,O',N,O^1;3\kappa^4O^1N',O'',O''')$ dinickel(II)sodium(I) pentahydrate, $[\text{NaNi}_2(\text{C}_{16}\text{H}_{14}\text{ClN}_2\text{O}_9)(\text{H}_2\text{O})_7]\cdot 5\text{H}_2\text{O}$ or $[\text{Ni}_2(\text{Cl-HXTA})(\text{H}_2\text{O})_4][\text{Na}(\text{H}_2\text{O})_3]\cdot 5\text{H}_2\text{O}$, the trinuclear complex unit consists of two distorted NiNO_5 octahedra bridged by a phenolate O atom and an NaO_4 tetrahedron bridged to one of the Ni octahedra by a carboxylate O atom. There are four intramolecular hydrogen bonds forming four six-membered rings in the complex and the complex molecules are connected to each other by a very complicated hydrogen-bond network.

Comment

In nickel enzymes, such as urease, Ni^{II} ions can catalyze the hydrolysis of urea (Jabri *et al.*, 1995). Cl-HXTA is a versatile 'end-off'-type acidic dinucleating ligand suitable for incorporating various dinuclear cores, first reported by Que and co-workers (Murch *et al.*, 1987). It functions as a pentavalent anionic ligand with four methoxycarbonyl chelating arms,



possessing two NO_3 coordination sites, and most of its dinuclear metal complexes are soluble in water. We report

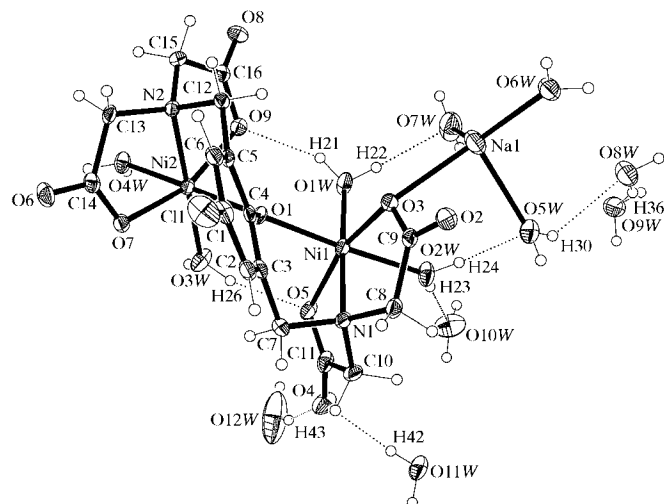


Figure 1

The structure of (I), with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii and hydrogen bonds are indicated by dotted lines.

here the crystal structure of the title trinuclear complex, (I), containing an Ni–O–Ni–O–Na bridge with Cl-HXTA.

Some features of the molecular geometry in (I) are presented in Table 1 and Fig. 1. In this trinuclear complex, both Ni^{2+} ions are located in similar coordination spheres. Each sphere has a distorted octahedral geometry comprised of two carboxylate groups, a tertiary N atom, two water molecules and a bridging phenolate O atom. This is in contrast with the structure of $[\text{Fe}_2(\text{HXTA})\text{OH}(\text{H}_2\text{O})_2]$ (Murch *et al.*, 1987), in which the coordination sphere of each Fe atom has the same geometry and coordination set and there are two bridges between the Fe^{II} cations.

The average Ni–O(phenolate) bond length in (I) is 2.051 Å and this compares well with the analogous bonds in other phenolate-bridged dimers (Chiari *et al.*, 1982, 1983). At each Ni^{2+} centre, the two water molecules and the tertiary N atom, as well as the bridging phenolate O atom, are almost coplanar. The $\text{Ni1}\cdots\text{Ni2}$ distance is 3.751 (1) Å, slightly longer than that in $[\text{Ni}_2(\text{Me}_4\text{-tpdp})(\text{MeCO}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ { $\text{Me}_4\text{-tpdp}$ is N,N,N',N' -tetrakis[(6-methyl-2-pyridyl)methyl]-1,3-diaminopropan-2-ol} (3.62 Å; Yamaguchi *et al.*, 2001). The $\text{Ni1}-\text{O1}-\text{Ni2}$ angle [132.2 (1)°] is much larger than the $\text{Fe1}-\text{O}-\text{Fe2}$ angle in $[\text{Fe}_2(\text{HXTA})\text{OH}(\text{H}_2\text{O})_2]$ (102.6°; Murch *et al.*, 1987), perhaps due to the presence of only one O-atom bridge between the two Ni^{2+} ions but two O-atom bridges between the two Fe^{2+} ions. Furthermore, in complex (I), atom O3 not only coordinates to atom Ni1 but also to an Na^+ ion, at a distance of 2.312 (3) Å. Therefore, atom O3 acts as a bridge between atoms Na1 and Ni1, with an $\text{Ni1}-\text{O}-\text{Na1}$ angle of 124.3 (2)°. The Na^+ ion completes its tetrahedral geometry with three other coordinated water molecules, with Na–O distances in the range 2.212 (3)–2.358 (4) Å. Thus, this complex is actually a trinuclear complex. The $\text{Ni1}\cdots\text{Na1}$ distance is 3.836 (2) Å.

The hydrogen-bonding geometry in (I) is listed in Table 2 and illustrated in Figs. 1 and 2. A number of intra- and

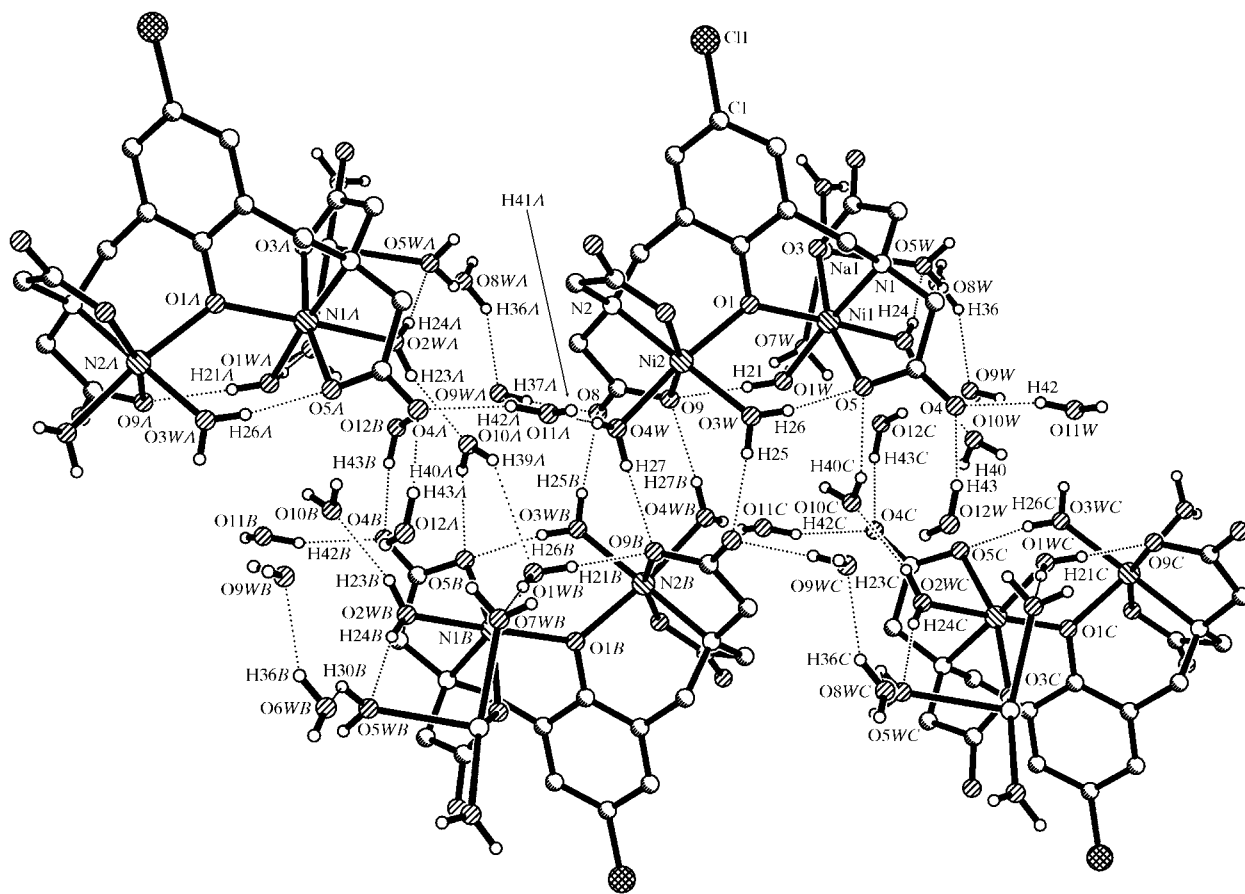


Figure 2

The hydrogen-bond network (dotted lines) of (I). Atoms labelled with the suffixes *A*, *B* or *C* are at the symmetry positions $(x, y - 1, z)$, $(1 - x, -y, 1 - z)$ or $(1 - x, 1 - y, 1 - z)$, respectively.

intermolecular hydrogen bonds stabilize the crystal structure. There are four intramolecular hydrogen bonds in the complex, namely $O3W-H3WA \cdots O5$, $O1W-H1WA \cdots O9$, $O1W-H1WB \cdots O7W$ and $O2W-H2WB \cdots O5W$, forming four six-membered rings (Fig. 1). In particular, water molecule $O1W$ is coordinated to atom $Ni1$, forming two hydrogen bonds *via* water molecule $O7W$ bonded to $Na1$ and atom $O9$ bonded to $Ni2$, making the complex more stable. Because four carboxylate groups and seven coordinated water molecules, as well as five non-coordinated water molecules, are included in this compound, a very complicated hydrogen-bond network (Fig. 2) is formed.

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China, and were used without further purification. The ligand Cl-HXTA was synthesized by a modification of the published procedures of Murch *et al.* (1987) and Branum *et al.* (2001). To an aqueous solution (100 ml) containing iminodiacetic acid (16.7 g, 0.125 mol) and *p*-chlorophenol (8.07 g, 0.063 mol) was added NaOH (10.5 g, 0.25 mol) in water (40 ml), and the mixture was cooled in an ice-water bath. Upon dissolution, 37% formaldehyde (15 ml) was added dropwise at 273 K. The solution was stirred for 30 min, heated at 343 K for 4 h, and then concentrated to

dryness. Recrystallization of the solid from methanol yielded light-yellow crystals of $Na_4(Cl-HXTA)$ (yield 90%). $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.496 g, 2.0 mmol) and $Na_4(Cl-HXTA)$ (0.516 g, 1.0 mmol) were dissolved in two aliquots of water (5 ml) and mixed with stirring at 323 K for 3 h. The resulting pale-green solution was filtered and the filtrate was left to stand at room temperature. Emerald-coloured crystals of the title compound appeared after 10 d by slow evaporation of the aqueous solvent.

Crystal data

$[NaNi_2(C_{16}H_{14}ClN_2O_9)(H_2O)_7] \cdot 5H_2O$
 $M_r = 770.34$
 Triclinic, $P\bar{1}$
 $a = 10.292(3) \text{ \AA}$
 $b = 11.564(3) \text{ \AA}$
 $c = 13.944(4) \text{ \AA}$
 $\alpha = 95.843(3)^\circ$
 $\beta = 109.438(3)^\circ$
 $\gamma = 103.123(3)^\circ$
 $V = 1495.4(7) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.711 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 2006 reflections
 $\theta = 2.4\text{--}25.2^\circ$
 $\mu = 1.45 \text{ mm}^{-1}$
 $T = 183(2) \text{ K}$
 Columnar, blue
 $0.40 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.594$, $T_{\max} = 0.868$
 6134 measured reflections

5126 independent reflections
 3733 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -12 \rightarrow 12$
 $k = -13 \rightarrow 12$
 $l = -16 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.081$
 $S = 1.00$
 5086 reflections
 388 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0188P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.89 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.72 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Na1—O6W	2.212 (3)	Ni1—N1	2.066 (3)
Na1—O3	2.312 (3)	Ni1—O2W	2.130 (3)
Na1—O5W	2.350 (3)	Ni1—Ni2	3.7508 (11)
Na1—O7W	2.358 (4)	Ni2—O3W	2.031 (3)
Na1—Ni1	3.836 (2)	Ni2—O1	2.041 (3)
Ni1—O3	2.025 (3)	Ni2—O7	2.047 (3)
Ni1—O1W	2.047 (3)	Ni2—N2	2.075 (3)
Ni1—O5	2.060 (3)	Ni2—O4W	2.081 (3)
Ni1—O1	2.061 (2)	Ni2—O9	2.106 (3)
O6W—Na1—O3	136.44 (14)	O1—Ni1—O2W	176.46 (12)
O6W—Na1—O5W	99.45 (13)	N1—Ni1—O2W	90.17 (13)
O3—Na1—O5W	89.55 (11)	O3W—Ni2—O1	85.72 (11)
O6W—Na1—O7W	124.55 (14)	O3W—Ni2—O7	95.86 (12)
O3—Na1—O7W	97.07 (13)	O1—Ni2—O7	95.19 (11)
O5W—Na1—O7W	93.02 (12)	O3W—Ni2—N2	178.87 (14)
O3—Ni1—O1W	99.39 (10)	O1—Ni2—N2	93.93 (11)
O3—Ni1—O5	163.68 (12)	O7—Ni2—N2	83.10 (12)
O1W—Ni1—O5	94.57 (10)	O3W—Ni2—O4W	89.21 (11)
O3—Ni1—O1	92.51 (10)	O1—Ni2—O4W	173.55 (11)
O1W—Ni1—O1	90.26 (10)	O7—Ni2—O4W	89.29 (11)
O5—Ni1—O1	95.86 (10)	N2—Ni2—O4W	91.21 (12)
O3—Ni1—N1	83.84 (12)	O3W—Ni2—O9	100.91 (12)
O1W—Ni1—N1	175.21 (10)	O1—Ni2—O9	92.69 (10)
O5—Ni1—N1	81.74 (12)	O7—Ni2—O9	161.94 (11)
O1—Ni1—N1	93.14 (12)	N2—Ni2—O9	80.17 (12)
O3—Ni1—O2W	86.61 (10)	O4W—Ni2—O9	84.34 (11)
O1W—Ni1—O2W	86.50 (12)	Ni2—O1—Ni1	132.22 (13)
O5—Ni1—O2W	85.84 (11)	Ni1—O3—Na1	124.26 (15)

The residual electron density had a maximum located 0.89 Å from atom H36. H atoms attached to C atoms were placed in geometrically idealized positions, with $Csp^3-H = 0.99 \text{ Å}$ and $Csp^2-H = 0.95 \text{ Å}$, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms attached to O atoms (water) were located in difference Fourier maps and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(O)$. The O—H distances are in the range 0.814–0.890 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2000); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H21...O9	0.83	2.00	2.766 (4)	153
O1W—H22...O7W	0.84	1.94	2.773 (4)	177
O2W—H23...O10W	0.82	1.96	2.767 (4)	167
O2W—H24...O5W	0.82	1.96	2.757 (4)	165
O3W—H25...O8 ⁱ	0.82	1.99	2.804 (4)	171
O3W—H26...O5	0.82	1.95	2.746 (4)	165
O4W—H27...O9 ⁱ	0.82	2.00	2.818 (4)	170
O4W—H28...O11W ⁱⁱ	0.82	1.83	2.652 (4)	177
O5W—H29...O2 ⁱⁱⁱ	0.84	1.89	2.711 (4)	166
O5W—H30...O8W	0.84	2.20	2.735 (4)	122
O6W—H31...O6 ^{iv}	0.84	1.90	2.741 (4)	177
O6W—H32...O6 ^v	0.84	1.99	2.810 (4)	167
O7W—H33...O12W ^{vi}	0.82	2.31	3.077 (6)	157
O7W—H34...O12W ^{vii}	0.82	1.86	2.656 (5)	164
O8W—H35...O7 ^v	0.81	2.02	2.805 (4)	162
O8W—H36...O9W	0.82	1.99	2.728 (5)	150
O9W—H37...O8 ^{viii}	0.82	1.98	2.787 (4)	167
O9W—H38...O8 ^{ix}	0.82	1.94	2.757 (4)	174
O10W—H39...O1W ^{xiii}	0.89	2.40	3.243 (3)	157
O10W—H40...O5 ^{vii}	0.83	2.31	2.915 (4)	130
O11W—H41...O8W ^x	0.82	2.11	2.830 (5)	146
O11W—H42...O4	0.82	1.92	2.728 (4)	166
O12W—H43...O4	0.82	1.86	2.636 (5)	157
O12W—H44...O9W ^{xii}	0.82	2.30	2.760 (5)	116

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1181). Services for accessing these data are described at the back of the journal.

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