

μ -1,4-Benzenedicarboxylato-bis[*trans*-aqua(1,4,8,11-tetraazacyclotetradecane)nickel(II)] diperchlorate forms a three-dimensional hydrogen-bonded frameworkChoudhury M. Zakaria,^{a†} George Ferguson,^b Alan J. Lough^c and Christopher Glidewell^{a*}^aSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, ^bDepartment of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and ^cLash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 3H6

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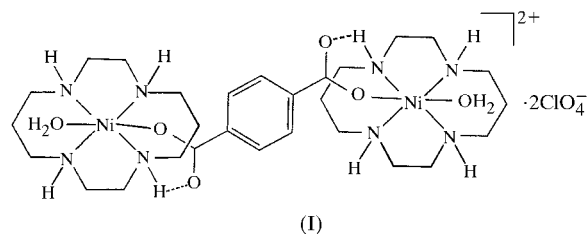
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The title compound, $[\text{Ni}_2(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_{24}\text{N}_4)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, contains two independent octahedral Ni^{II} centres with *trans*- NiN_4O_2 chromophores. The bridging benzenedicarboxylate ligand is bonded to the two Ni atoms, each *via* one O atom of each carboxylate, while the other O atom participates in an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond, forming an *S*(6) motif. The cations are linked to the perchlorate anions *via* $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds [$\text{O}\cdots\text{O}$ 2.904 (6) and 2.898 (6) Å; $\text{O}-\text{H}\cdots\text{O}$ 158 (6) and 165 (6)°; $\text{N}\cdots\text{O}$ 3.175 (7) and 3.116 (7) Å; $\text{N}-\text{H}\cdots\text{O}$ 168 and 166°] to form molecular ladders. These ladders are linked by further $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds [$\text{O}\cdots\text{O}$ 2.717 (6) and 2.730 (5) Å; $\text{O}-\text{H}\cdots\text{O}$ 170 (4) and 163 (6)°; $\text{N}\cdots\text{O}$ 3.373 (7) and 3.253 (7) Å; $\text{N}-\text{H}\cdots\text{O}$ 163 and 167°] to form a continuous three-dimensional framework. The perchlorate anions both participate in three hydrogen bonds, and both are thus fully ordered.

Comment

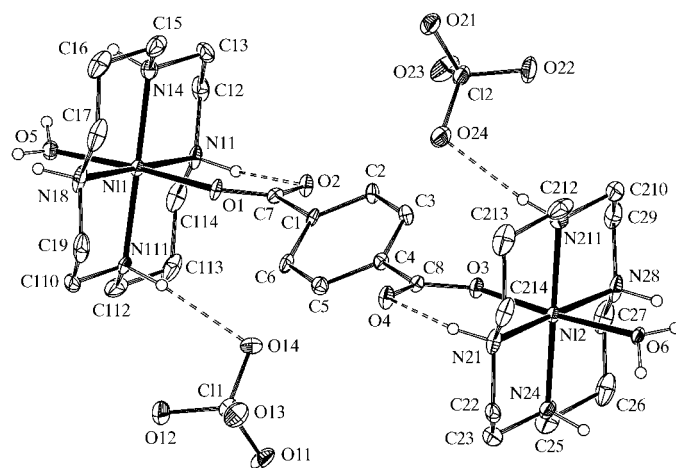
The $[\text{Ni}(\text{cyclam})]^{2+}$ cation [(1,4,8,11-tetraazacyclotetradecane)nickel(II)], $[\text{Ni}(\text{C}_{10}\text{H}_{24}\text{N}_4)]^{2+}$, reacts readily with two equivalents of the 4-hydroxybenzoate anion to yield a neutral complex containing a *trans*-octahedral NiN_4O_2 chromophore (Glidewell *et al.*, 2000). In this complex, $[(\text{HOC}_6\text{H}_4\text{COO})_2\text{Ni}(\text{cyclam})]$, the square-planar $[\text{Ni}(\text{cyclam})]$ fragment has two axial sites available for coordination, in this case by the hydroxybenzoate ligands, and a well defined array of axial $\text{N}-\text{H}$ bonds, two on each face of the nearly planar macrocycle, available for hydrogen-bond formation. The $[\text{Ni}(\text{cyclam})]^{2+}$

cation is thus an attractive building block for the construction of predesigned coordination polymer networks, using, for example, polycarboxylate anions as the axial ligands. It is reasonable to envisage that growth of coordination polymer networks proceeds in a stepwise fashion *via* low- and medium-molecularity intermediates. By use of the 1,4-benzenedicarboxylate (terephthalate) anion, $[\text{C}_6\text{H}_4(\text{COO})_2]^{2-}$, we have now isolated the title anion-bridged dinuclear complex, (I), and its structure is presented here.



In the cation of (I) (Fig. 1), the bridging dianionic ligand utilizes one O atom of each carboxylate group to coordinate to the Ni atom, while the other O atom in each group accepts a hydrogen bond, forming an *S*(6) motif, precisely as observed in the 4-hydroxybenzoate complex (Glidewell *et al.*, 2000). This coordination mode, with direct $\text{Ni}-\text{O}$ bonds to the carboxylate anion, differs from that observed with 1,3,5-benzenetricarboxylate, where the anions are simply hydrogen-bonded to *trans*- $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$ cations (Choi *et al.*, 1999). Each Ni atom is also coordinated by four N atoms from the cyclam ligand, which occupy the equatorial sites of an axially elongated octahedron. A water molecule occupies the second axial site of each Ni atom.

The cyclam ligands adopt the usual *trans*-III conformation (Barefield, Bianchi *et al.*, 1986), with all torsion angles in the ring within 15° of either 180° (antiperiplanar) or ±60° (synclinal) (Table 1). The $\text{Ni}-\text{N}$ distances are closely similar, ranging only from 2.049 (5) to 2.089 (5) Å; these distances are typical of those observed in octahedral Ni^{II} complexes of

**Figure 1**

The asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity, except those on N atoms and in water molecules, which are shown as small spheres of arbitrary radii.

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cyclam and its C-methyl derivatives (Whimp *et al.*, 1970; Curtis *et al.*, 1973; Hay *et al.*, 1982; Ito *et al.*, 1984; Barefield, Bianchi *et al.*, 1986; Barefield, Freeman & Van Derveer, 1986; Hambley, 1986; Mochizuki & Kondo, 1995; Choi *et al.*, 1999; Glidewell *et al.*, 2000), although they are significantly shorter than those observed in the square-planar systems (Prasad & McAuley, 1983; Barefield, Bianchi *et al.*, 1986; Adam *et al.*, 1991). The mean value of the Ni–O distances, 2.161 (4) Å, is virtually identical with those observed in salts of *trans*-[Ni(cyclam)(H₂O)₂]²⁺ cations (Mochizuki & Kondo, 1995; Choi *et al.*, 1999). On the other hand, the C–N distances exhibit a much wider range, from 1.431 (9) to 1.524 (9) Å.

Although the two [Ni(cyclam)] fragments in the cation are fully eclipsed with respect to the Ni··Ni vector, the detailed differences in the C–N distances and in the magnitudes of the torsion angles involving corresponding sets of atoms in the two [Ni(cyclam)] fragments prevent the cation from attaining a centrosymmetric configuration. Nonetheless, the O–Ni(N₄)–benzenedicarboxylato–Ni(N₄)–O unit (*i.e.* the entire cation except for the C atoms of the cyclam ligands) is very close to being centrosymmetric. In the bridging ligand, the carboxylate groups based on C7 and C8 are rotated out of the plane of the aryl ring by 38.0 (2) and 35.2 (2)°, respectively, with the sense of the rotations mimicking centrosymmetry (Fig. 1).

The two perchlorate anions are both fully ordered. Each participates in three hydrogen bonds (Table 2), and it is these which prevent the almost free rotation often observed with this anion. Within the selected asymmetric unit (Fig. 1), N111 and N211 act as hydrogen-bond donors to O14 and O24, respectively (Table 2).

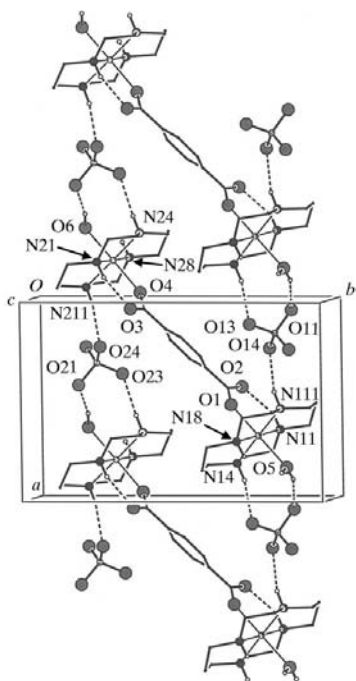


Figure 2
Part of the crystal structure of (I), showing the formation of a molecular ladder parallel to [100]. H atoms bonded to C atoms have been omitted for clarity.

Apart from the formation of the four N–H··O hydrogen bonds within the selected asymmetric unit, the cation of (I) has four N–H and four O–H bonds available for the formation of hydrogen bonds to other aggregates. Four of the resulting hydrogen bonds (entries 5–8 in Table 2) link the three-ion aggregates into chains running parallel to the [100] direction, while the other four (entries 9–12 in Table 2) link each [100] to four of its neighbours, so generating a continuous three-dimensional framework. Atom N14 in the cation at (x, y, z) acts as a donor to perchlorate atom O13 at $(1 + x, y, z)$, while atom O5 at (x, y, z) acts as a donor, *via* H52, to O11 in the same perchlorate at $(1 + x, y, z)$. In an entirely similar manner, atoms N24 and O6 at (x, y, z) act as donors to O23 and O21, respectively, at $(x - 1, y, z)$, so forming a molecular ladder parallel to [100] in which each upright is a C(8)C(8)[R₂²(8)] chain of rings, while the Ni–benzenedicarboxylato–Ni units form the rungs (Fig. 2). This ladder runs approximately along the line $(x, \frac{1}{2}, \frac{1}{4})$ and a second similar ladder runs approximately along the line $(x, 0, \frac{3}{4})$. Each ladder is directly linked to four neighbouring ladders: atoms N18 and O5 at (x, y, z) , which are components of the ladder along $(x, \frac{1}{2}, \frac{1}{4})$, both act as hydrogen-bond donors to O4 at $(1 - x, \frac{1}{2} + y, 1 - z)$, which is a component of the ladder along $(x, 1, \frac{3}{4})$. Similarly, atoms N28 and O6 at (x, y, z) both act as donors to O2 at $(-x, y - \frac{1}{2}, -z)$, which is a component of the ladder along $(x, 0, -\frac{1}{4})$. In this manner, the ladder along $(x, \frac{1}{2}, \frac{1}{4})$ is directly linked to the four ladders along $(x, 0, \frac{3}{4})$, $(x, 0, -\frac{1}{4})$, $(x, 1, \frac{3}{4})$ and $(x, 1, -\frac{1}{4})$ (Fig. 3), and propagation of these hydrogen bonds by the space group links all of the [100] ladders into a three-dimensional framework.

In addition to the O–H··O and N–H··O hydrogen bonds, there are also four significant C–H··O hydrogen bonds. Two of these (entries 13 and 14 in Table 2) reinforce the

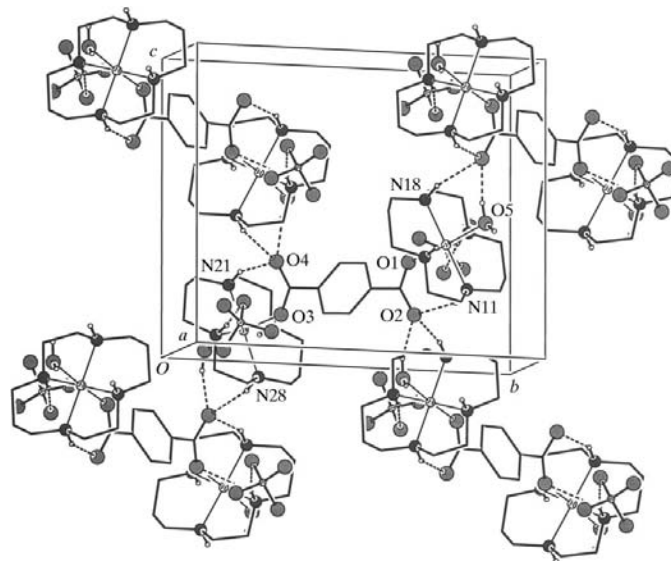


Figure 3
Part of the crystal structure of (I) showing the linking of the [100] molecular ladders into a three-dimensional framework. H atoms bonded to C atoms have been omitted for clarity.

[100] chains, while the other two reinforce the links between these chains.

For the two intra-cation N—H···O hydrogen bonds, the short N···O distances are probably largely determined by the adjacent Ni—O coordination. The remainder of the N—H···O hydrogen bonds fall into two clear groups (Table 2); those having perchlorate O atoms as acceptors have significantly shorter N···O distances than those having carboxylate O atoms as acceptors. By contrast, the O—H···O hydrogen bonds with perchlorate O atoms as acceptors have significantly longer O···O distances than those with carboxylate O-atom acceptors. The D—H···A angles for the hard inter-ion hydrogen bonds are all closely clustered around the mean value of 166°. Hence, the pattern of H···A distances closely follows that of the D···A distances.

Experimental

A sample of compound (I) was isolated as a purple microcrystalline solid from the reaction between [Ni(cyclam)](ClO₄)₂ and the disodium salt of terephthalic acid in aqueous methanol. Crystals of (I) suitable for single-crystal X-ray diffraction were grown from a solution in water.

Crystal data

[Ni ₂ (C ₈ H ₄ O ₄)(C ₁₀ H ₂₄ N ₄) ₂ (H ₂ O) ₂](ClO ₄) ₂	$D_x = 1.557 \text{ Mg m}^{-3}$
$M_r = 917.09$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 7654 reflections
$a = 10.2842 (3) \text{ \AA}$	$\theta = 2.8\text{--}27.5^\circ$
$b = 14.9172 (4) \text{ \AA}$	$\mu = 1.17 \text{ mm}^{-1}$
$c = 13.0621 (4) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 102.5220 (11)^\circ$	Plate, purple
$V = 1956.21 (10) \text{ \AA}^3$	$0.18 \times 0.18 \times 0.07 \text{ mm}$
$Z = 2$	

Data collection

KappaCCD diffractometer	7654 independent reflections
φ and ω scans with κ offsets	5458 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.052$
$T_{\text{min}} = 0.817$, $T_{\text{max}} = 0.922$	$\theta_{\text{max}} = 27.5^\circ$
13 566 measured reflections	$h = -13 \rightarrow 13$
	$k = -19 \rightarrow 17$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.019P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
7654 reflections	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
501 parameters	Absolute structure: Flack (1983)
H atoms treated by a mixture of independent and constrained refinement	Flack parameter = 0.38 (3)

Compound (I) crystallized in the monoclinic system, and space group $P2_1$ or $P2_1/m$ was indicated by the systematic absences. $P2_1$ was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H = 0.95 (aromatic) and 0.99 Å (aliphatic CH₂), and N—H = 0.93 Å. Water H atoms were clearly visible in difference maps and were initially refined isotropically using a *DFIX* command (*SHELXL97*; Sheldrick, 1997), with a free variable for the common O—H distance and a free variable for the overall U_{iso} value. The final refinement had the water O—H distance set to 0.85 Å. Refinement of

Table 1

Selected geometric parameters (Å, °).

Ni1—Ni11	2.072 (5)	Ni2—N21	2.049 (5)
Ni1—Ni14	2.071 (5)	Ni2—N24	2.070 (5)
Ni1—N18	2.077 (5)	Ni2—N28	2.089 (5)
Ni1—N111	2.062 (5)	Ni2—N211	2.057 (6)
Ni1—O1	2.106 (4)	Ni2—O3	2.125 (4)
Ni1—O5	2.211 (4)	Ni2—O6	2.202 (4)
N11—C114	1.474 (8)	N21—C214	1.464 (8)
N11—C12	1.459 (8)	N21—C22	1.491 (7)
N14—C13	1.494 (8)	N24—C23	1.463 (8)
N14—C15	1.457 (8)	N24—C25	1.493 (8)
N18—C17	1.524 (9)	N28—C27	1.431 (9)
N18—C19	1.467 (9)	N28—C29	1.521 (9)
N111—C110	1.499 (7)	N211—C210	1.491 (7)
N111—C112	1.441 (8)	N211—C212	1.490 (9)
N11—C12—C13—N14	−55.8 (7)	N21—C22—C23—N24	55.6 (6)
C12—C13—N14—C15	169.6 (5)	C22—C23—N24—C25	−170.7 (5)
C13—N14—C15—C16	−179.0 (5)	C23—N24—C25—C26	178.6 (5)
N14—C15—C16—C17	73.8 (7)	N24—C25—C26—C27	−72.8 (7)
C15—C16—C17—N18	−72.2 (7)	C25—C26—C27—N28	74.6 (7)
C16—C17—N18—C19	175.7 (5)	C26—C27—N28—C29	−178.3 (5)
C17—N18—C19—C110	−172.1 (5)	C27—N28—C29—C210	170.0 (5)
N18—C19—C110—N111	59.5 (7)	N28—C29—C210—N211	−58.3 (6)
C19—C110—N111—C112	−170.1 (6)	C29—C210—N211—C212	171.1 (5)
C110—N111—C112—C113	−179.3 (5)	C210—N211—C212—C213	−178.8 (5)
N111—C112—C113—C114	−70.2 (8)	N211—C212—C213—C214	71.1 (8)
C112—C113—C114—N11	70.2 (7)	C212—C213—C214—N21	−71.7 (8)
C113—C114—N11—C12	180.0 (5)	C213—C214—N21—C22	−178.7 (4)
C114—N11—C12—C13	167.6 (5)	C214—N21—C22—C23	−170.3 (5)

the Flack parameter (Flack, 1983) using 3083 Friedel-related reflections suggested that the data should be treated as a racemic twin, using the *TWIN* and *BASF* commands in *SHELXL97*. The structure of (I) approximates closely to a centrosymmetric one, with the terephthalate moiety lying about an inversion centre in space group $P2_1/n$. There is an almost perfect fit of atoms, except for all the C and H atoms of the cyclam residues. Inspection of the reflection data shows clearly that the $h0l$ glide reflections ($h + l = 2n + 1$), which would be absent in $P2_1/n$, are clearly present, although many are weak.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure:

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···O2	0.93	2.09	2.939 (6)	151
N21—H21···O4	0.93	2.06	2.920 (7)	154
N111—H111···O14	0.93	2.27	3.183 (7)	165
N211—H211···O24	0.93	2.22	3.135 (7)	170
N14—H14···O13 ⁱ	0.93	2.26	3.175 (7)	168
O5—H52···O11 ⁱ	0.85 (5)	2.10 (5)	2.904 (6)	158 (6)
N24—H24···O23 ⁱⁱ	0.93	2.20	3.116 (7)	166
O6—H62···O21 ⁱⁱ	0.85 (4)	2.07 (4)	2.898 (6)	165 (6)
N18—H18···O4 ⁱⁱⁱ	0.93	2.47	3.373 (7)	163
O5—H51···O4 ⁱⁱⁱ	0.85 (2)	1.88 (2)	2.717 (6)	170 (4)
N28—H28···O2 ^{iv}	0.93	2.34	3.253 (7)	167
O6—H61···O2 ^{iv}	0.85 (2)	1.91 (2)	2.730 (5)	163 (6)
C12—H12A···O11 ⁱ	0.99	2.44	3.372 (8)	157
C22—H22A···O21 ⁱⁱ	0.99	2.43	3.402 (7)	166
C19—H19A···O24 ⁱⁱⁱ	0.99	2.41	3.273 (8)	146
C29—H29A···O14 ^{iv}	0.99	2.56	3.402 (7)	142

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

SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1465). Services for accessing these data are described at the back of the journal.

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