Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(4-hydroxybenzoato-*O*)(1,4,8,11-tetraazacyclotetradecane-κ^4N)-nickel(II): a three-dimensional framework built from O—H···O and N—H···O hydrogen bonds

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Received 22 October 1999
Accepted 4 November 1999

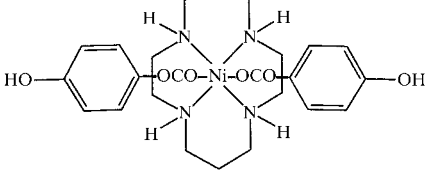
The title compound, $[Ni(C_7H_5O_3)_2(C_{10}H_{24}N_4)]$, contains octahedral Ni^{II} in a centrosymmetric *trans* configuration with Ni—N distances of 2.0637 (17) and 2.0699 (16) Å and an Ni—O distance of 2.1100 (14) Å. The molecules are linked by a single type of O—H···O hydrogen bond [O···O 2.618 (2) Å and O—H···O 161°] into two-dimensional sheets; a single type of N—H···O hydrogen bond [N···O 2.991 (2) Å and N—H···O 139°] links these sheets into a three-dimensional framework.

Comment

The tetraaza macrocycles 1,4,8,11-tetraazacyclotetradecane (cyclam, $C_{10}H_{24}N_4$) and its hexa-C-methyl analogue 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane [tet-a (*meso* form) and tet-b (racemic), $C_{16}H_{36}N_4$] form adducts with oxygen-containing hydrogen-bond donors which exhibit a wide range of supramolecular architectures (Ferguson *et al.*, 1998, 1999; Gregson *et al.*, 2000; Lough *et al.*, 2000). However, despite the great structural variety exhibited by these adducts, a common feature is the formation by double proton capture of the dications $(C_{10}H_{26}N_4)^{2+}$ and $(C_{16}H_{38}N_4)^{2+}$ in which two protons are held within the N_4 cavity by means of N—H···N hydrogen bonds. Associated with this intramolecular constraint is the adoption by the macrocycles of the fairly rigid and nearly planar *trans*-III conformation (Barefield, Bianchi *et al.*, 1986).

Both of these macrocycles form nickel(II) complexes in which the coordination of the metal may be either square planar (Prasad & McAuley, 1983; Barefield, Bianchi *et al.*, 1986; Adam *et al.*, 1991) or, in the presence of two additional ligands, octahedral; in the octahedral complexes, the two additional ligand sites may be mutually *trans* when the *trans*-III conformation of the macrocyclic ligand is retained (Ito *et al.*, 1984; Mochizuki & Kondo, 1995; Choi *et al.*, 1999) or mutually *cis* when the macrocycle is necessarily heavily folded (Whimp *et al.*, 1970; Curtis *et al.*, 1973; Barefield, Bianchi *et al.*, 1986). Entirely similar properties are exhibited by the tetra-C-methyl derivative of cyclam (Hay *et al.*, 1982; Barefield, Freeman & Van Derveer, 1986; Hambley, 1986) confirming that the behaviour of the macrocycle is independent of the degree of C-methyl substitution.

In view of both the configurational versatility of a cation such as $[Ni(cyclam)]^{2+}$ and the great structural diversity of the metal-free macrocycles in supramolecular chemistry (Ferguson *et al.*, 1998, 1999; Gregson *et al.*, 2000; Lough *et al.*, 2000), it is of interest to investigate the behaviour of $[Ni(cyclam)]^{2+}$ with oxygen-containing hydrogen-bond donors which themselves contain sufficient additional hydrogen-bonding capacity to generate supramolecular aggregates. Anionic ligands L could, in principle, be attached to the $[Ni(cyclam)]^{2+}$ cation either *via* Ni—L coordinate bonds, *via* N—H···L hydrogen bonds or by some combination of the two, thus affording the possibility of either square-planar or octahedral Ni^{II}. We report here the structural characterization of one such adduct, $[Ni(C_{10}H_{24}N_4)]^{2+}\cdot 2[(HOC_6H_4COO)^-]$, (I), formed with 4-hydroxybenzoic acid.



(I)

In compound (I), the Ni atom adopts a *trans*-octahedral configuration (Fig. 1) with 4-hydroxybenzoate anions acting as the axial ligands. The molecules lie across centres of inversion in $P2_1/n$ giving a pseudo-I arrangement of Ni atoms. The axial 4-hydroxybenzoate ligands bind to the metal in only a monodentate fashion, although they are also connected to the cyclam ligand by means of N—H···O hydrogen bonds (Fig. 1 and Table 2), so generating a novel $S(6)$ synthon (Bernstein *et*

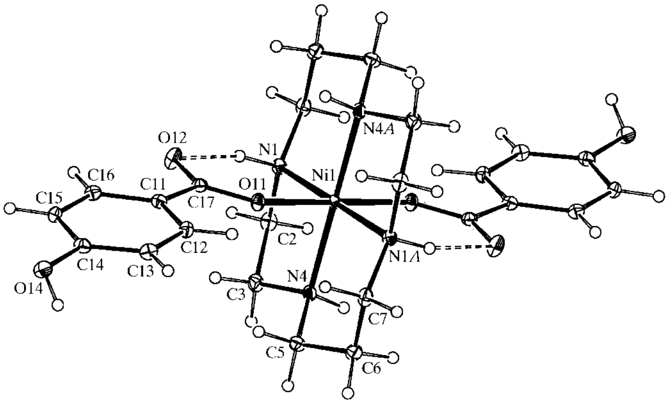


Figure 1
A view of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

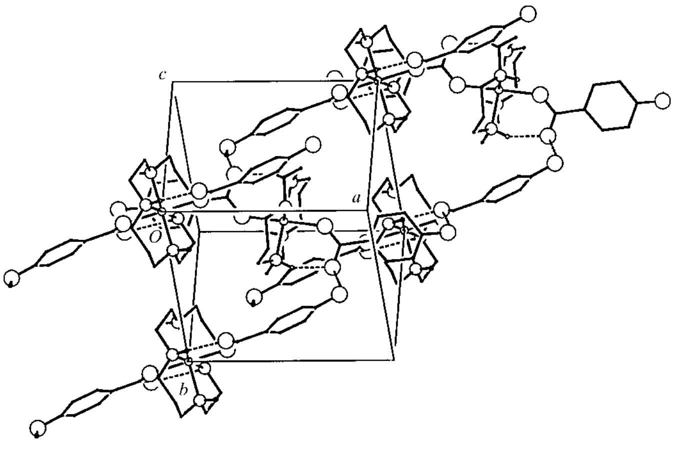


Figure 2
Part of the crystal structure of (I) showing the formation of a $(10\bar{1})$ sheet built from $R_4^4(40)$ rings.

al., 1995; Desiraju, 1995). By contrast, in the salt formed between the *trans*-$[Ni(cyclam)(H_2O)_2]^{2+}$ cation and the trianion of benzene-1,3,5-tricarboxylic acid, the cations and anions are linked solely by O—H···O hydrogen bonds in which water ligands act as hydrogen-bond donors (Choi *et al.*, 1999). It is noteworthy that in both the cations $[Ni(tet\text{-}b)OCOCH_3]^+$ (Whimp *et al.*, 1970) and $[Ni(tet\text{-}a)(acac)]^+$ (Curtis *et al.*, 1973) $[(acac)^- = (CH_3COCHCOCH_3)^-]$ the oxygen ligands are each bound to Ni in a bidentate fashion so that the two O sites are mutually *cis* and the macrocycle is folded; indeed the $[Ni(tet\text{-}a)(acac)]^+$ cations lie on twofold rotation axes. On the other hand, when H_2O molecules act as the additional ligands, both *cis* (folded) and *trans* (planar) configurations of the cation $[Ni(cyclam)(H_2O)_2]^{2+}$ can be observed (Barefield, Bianchi *et al.*, 1986; Mochizuki & Kondo, 1995; Choi *et al.*, 1999).

The Ni—N distances in (I) (Table 1) are typical of those observed in octahedral Ni^{II} complexes of 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), but significantly shorter than those observed in the square-planar systems (Prasad & McAuley, 1983; Barefield, Bianchi *et al.*, 1986; Adam *et al.*, 1991). The unique Ni—O distance in (I) is a little shorter than those observed in $[Ni(cyclam)(H_2O)_2]^{2+}$ cations. In the chloride salt of the *cis* isomer, the values are 2.130 (2) and 2.140 (1) Å (Barefield, Bianchi *et al.*, 1986) and for the centrosymmetric *trans* isomer the unique Ni—O distance is 2.176 (2) Å in the chloride salt (Mochizuki & Kondo, 1995) and 2.160 (3) Å in the benzene-1,3,5-tricarboxylate salt (Choi *et al.*, 1999). The shorter bond in (I) possibly arises from the anionic nature of the axial ligand; this is supported by the Ni—O distances in the acetato complex $[Ni(tet\text{-}b)OCOCH_3]^+$ [2.103 (9) and 2.116 (9) Å; Whimp *et al.*, 1970].

Within the macrocyclic ligand, the torsional angles (Table 1) indicate almost perfect staggering about all the C—C and C—N bonds, as expected for the *trans*-III conformation (Barefield, Bianchi *et al.*, 1986); as usual in this conformation, there are four axial N—H bonds which are almost normal to the mean plane of the macrocycle, two on each face. One symmetry-related pair of these bonds is engaged in forming intramolecular N—H···O hydrogen bonds; the other pair forms intermolecular N—H···O hydrogen bonds. In the anion, the carboxylate group is twisted out of the plane of the aryl ring by 8.2 (2)°.

A combination of O—H···O and N—H···O hydrogen bonds (Table 2) links the neutral molecules (Fig. 1) into a continuous three-dimensional framework. It simplifies considerably the structural description if the effects of the O—H···O and N—H···O hydrogen bonds are treated separately. A single type of intermolecular O—H···O hydrogen bond serves to link the molecules into two-dimensional nets lying parallel to the $(10\bar{1})$ plane (Fig. 2) and built from a single type of centrosymmetric $R_4^4(40)$ ring. The hydroxyl O14 at (x, y, z) acts as donor to the carboxylate O12 at $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, so producing a $C(8)$ chain parallel to the [101] direction and generated by the glide plane; the action of the centres of inversion upon these chains generates the two-dimensional net. The molecule centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is a donor of O—H···O hydrogen bonds to the pair of molecules centred at (0,0,0) and (1,1,1), and an acceptor of O—H···O hydrogen bonds from the molecules centred at (0,1,0) and (1,0,1). Just one net of this type is sufficient to account for all the unit-cell contents.

The continuous stack of parallel nets is linked into a three-dimensional framework by chains running parallel to the [100] direction; N4 at (x, y, z) acts as donor to the hydroxylic O14 at $(-1 + x, y, z)$ and propagation of this interaction by the space group generates a $C(10)[R_2^2(20)]$ chain-of-rings (Bernstein *et al.*, 1995), where the rings are centred at $(n,\frac{1}{2},\frac{1}{2})$ (n = zero or integer) (Fig. 3). Thus, just two types of intermolecular hydrogen bond serve to link all the molecules into a single supramolecular aggregate. Although the aryl ring planes of the 4-hydroxybenzoate ligands in neighbouring molecules are separated by only *ca* 3.59 Å, the centroid offset effectively precludes the occurrence of any aromatic $\pi\cdots\pi$ stacking interactions between these rings.

The orange–brown colour of (I) is that commonly associated with diamagnetic square-planar Ni^{II}, although in (I) the coordination of the Ni is metrically octahedral. The Angular Overlap Model (Burdett, 1980) readily shows that spin-pairing in metrically octahedral d^8 complexes of type *trans*-MX_4Y_2 is possible, provided only that the ligand-field characteristics of

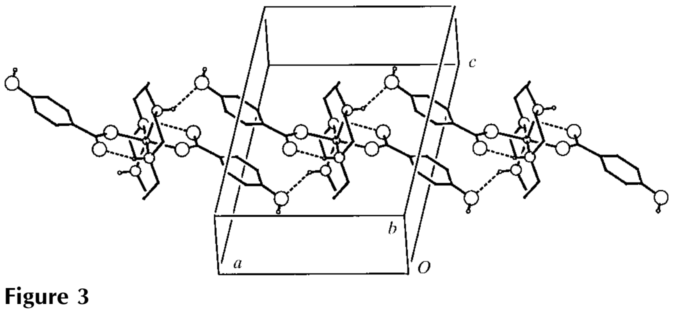


Figure 3
Part of the crystal structure showing the $C(10)[R_2^2(20)]$ chain-of-rings parallel to the [100] direction.

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the equatorial and axial ligands *X* and *Y* are sufficiently different.

Experimental

Stoichiometric quantities of [Ni(cyclam)]$(ClO_4)_2$ and the sodium salt of 4-hydroxybenzoic acid were separately dissolved in water. The solutions were mixed and set aside to crystallize, producing orange–brown crystals of compound (I). Analysis: found C 54.0, H 6.2, N 10.4%; $C_{24}H_{34}N_4NiO_6$ requires C 54.0, H 6.4, N 10.5%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$[Ni(C_7H_5O_3)_2(C_{10}H_{24}N_4)]$
$M_r = 533.26$
Monoclinic, $P2_1/n$
$a = 10.8397\ (6)$ Å
$b = 8.7317\ (6)$ Å
$c = 12.8670\ (9)$ Å
$\beta = 102.160\ (4)^\circ$
$V = 1190.52\ (13)$ Å^3
$Z = 2$
$D_x = 1.488$ Mg m^{-3}
Mo Kα radiation
Cell parameters from 2696 reflections
$\theta = 2.76$–27.56°
$\mu = 0.864$ mm^{-1}
$T = 100\ (1)$ K
Plate, orange–brown
$0.40 \times 0.35 \times 0.10$ mm

Data collection

KappaCCD diffractometer
φ and ω scans with κ offset scans
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.724$, $T_{max} = 0.919$
19 420 measured reflections
2696 independent reflections
2124 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 27.56^\circ$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 11$
$l = -16 \rightarrow 16$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.089$
$S = 1.027$
2696 reflections
161 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.7434P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.411$ e Å^{-3}
$\Delta\rho_{min} = -0.405$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	2.0699 (16)	N1—C2	1.474 (3)
Ni1—N4	2.0637 (17)	C2—C3	1.525 (3)
Ni1—O11	2.1100 (14)	C3—N4	1.474 (3)
O11—C17	1.263 (2)	N4—C5	1.478 (3)
O12—C17	1.265 (2)	C5—C6	1.524 (3)
O14—C14	1.373 (2)	C6—C7	1.520 (3)
C11—C17	1.503 (3)	C7—N1^{i}	1.478 (3)
N1—Ni1—N4	85.29 (7)	C7^{i}—N1—C2	113.82 (16)
N1—Ni1—O11^{i}	86.29 (6)	N1—C2—C3	108.76 (17)
N4—Ni1—O11	92.07 (6)	C2—C3—N4	108.61 (17)
O14—C14—C13	121.63 (19)	C3—N4—C5	113.27 (16)
O14—C14—C15	118.23 (19)	N4—C5—C6	111.15 (17)
O11—C17—O12	124.62 (18)	C5—C6—C7	115.98 (18)
O11—C17—C11	116.78 (18)	C6—C7—N1^{i}	112.03 (17)
O12—C17—C11	118.54 (18)		
C7^{i}—N1—C2—C3	169.9 (2)	N4—C5—C6—C7	71.6 (2)
N1—C2—C3—N4	−56.4 (2)	C5—C6—C7—N1^{i}	−71.4 (2)
C2—C3—N4—C5	169.7 (2)	C6—C7—N1^{i}—C2^{i}	178.5 (2)
C3—N4—C5—C6	−179.9 (2)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O12	0.93	2.06	2.909 (2)	152
N4—H4$\cdots$O14^{i}	0.93	2.23	2.991 (2)	139
O14—H14$\cdots$O12^{ii}	0.84	1.81	2.618 (2)	161

Symmetry codes: (i) $x - 1, y, z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

All H atoms were clearly resolved in difference maps and were treated as riding atoms in the refinement with C—H 0.95 and 0.99, N—H 0.93 and O—H 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: Patterson heavy-atom method and *SHELXL*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada. RMG thanks EPSRC (UK) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1344). Services for accessing these data are described at the back of the journal.

References

Adam, K. R., Antolovich, M., Brigden, L. G., Leong, A. J., Lindoy, L. F., Baillie, P. J., Uppal, D. K., McPartlin, M., Shah, B., Proserpio, D., Fabbrizzi, L. & Tasker, P. A. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2493–2501.

Barefield, E. K., Bianchi, A., Billo, E. J., Connolly, P. J., Paoletti, P., Summers, J. S. & Van Derveer, D. G. (1986). *Inorg. Chem.* **25**, 4197–4202.

Barefield, E. K., Freeman, G. M. & Van Derveer, D. G. (1986). *Inorg. Chem.* **25**, 552–558.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Burdett, J. K. (1980). In *Molecular Shapes*. New York: Wiley.

Choi, H. J., Lee, T. S. & Suh, M. P. (1999). *Angew. Chem. Int. Ed. Engl.* **38**, 1405–1408.

Curtis, N. F., Swann, D. A. & Waters, T. N. (1973). *J. Chem. Soc. Dalton Trans.* pp. 1408–1413.

Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998). *Acta Cryst.* B**54**, 139–150.

Ferguson, G., Gregson, R. M. & Glidewell, C. (1999). *Acta Cryst.* C**55**, 815–817.

Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst.* B**56**. In the press.

Hambley, T. W. (1986). *J. Chem. Soc. Dalton Trans.* pp. 565–569.

Hay, R. W., Jeragh, B., Ferguson, G., Kaitner, B. & Ruhl, B. L. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1531–1539.

Ito, T., Kato, M. & Ito, H. (1984). *Bull. Chem. Soc. Jpn*, **57**, 2641–2649.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lough, A. J., Gregson, R. M., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* B**56**. In the press.

Mochizuki, K. & Kondo, T. (1995). *Inorg. Chem.* **34**, 6241–6243.

Nonius (1997). *KappaCCD Server Software*. Windows 3.11. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Prasad, L. & McAuley, A. (1983). *Acta Cryst.* C**39**, 1175–1177.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1999). *PLATON*. Version of October 1999. University of Utrecht, The Netherlands.

Whimp, P. O., Bailey, M. F. & Curtis, N. F. (1970). *J. Chem. Soc. A*, pp. 1956–1963.