

meso-5,5,7,12,12,14-Hexamethyl-1,4-diaza-8,11-diazoniacyclotetradecane bis(2-naphthoate) ethanol disolvate: centrosymmetric five-component aggregates linked into sheets by C—H··· π (arene) hydrogen bonding

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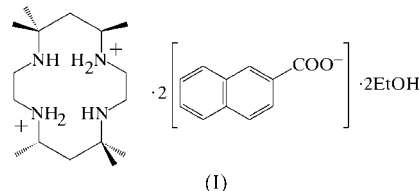
The title compound is an ethanol-solvated salt, $C_{16}H_{38}N_4^{2+} \cdot 2C_{11}H_7O_2^- \cdot 2C_2H_6O$, in which the cation lies across a centre of inversion in $P2_1/c$. The ions are linked by N—H···O hydrogen bonds [$H \cdots O = 1.70$ and 2.30 \AA , $N \cdots O = 2.624$ (2) and 3.136 (2) \AA , and $N-H \cdots O = 178$ and 151°], and the ethanol molecule is linked to the anion by an O—H···O hydrogen bond [$H \cdots O = 1.90 \text{ \AA}$, $O \cdots O = 2.728$ (2) \AA and $O-H \cdots O = 171^\circ$], to form a centrosymmetric five-component aggregate. C—H···O hydrogen bonds and aromatic π – π -stacking interactions are absent, but the aggregates are linked into sheets by a single C—H··· π (arene) hydrogen bond.

Comment

The nickel(II) complex $[(RCOO)_2Ni(\text{cyclam})]$, where $RCOO^-$ represents 2-naphthoate, $C_{10}H_7COO^-$, and cyclam is 1,4,8,11-tetraazacyclotetradecane, $C_{10}H_{24}N_4$, is centrosymmetric, with naphthoate ligands occupying mutually *trans* sites in an octahedral NiN_4O_2 chromophore (Zakaria *et al.*, 2002). An unexpected feature of this structure is the complete absence of aromatic π – π -stacking interactions between the naphthalene rings in adjacent complexes, even though the closest approach between these rings is across a centre of inversion, so that the rings involved are strictly parallel. While the shortest interplanar spacing between such rings is only 3.122 (2) \AA , the corresponding distance between the ring centroids is 5.260 (2) \AA , with a corresponding centroid offset of 4.233 (2) \AA , so that there is no ring overlap whatsoever.

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Intrigued by this feature, we have now studied a related 2-naphthoic acid derivative, *viz.* the title ethanol-solvated adduct, (I), formed between this acid and tet-a (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). The constitution of (I) (Fig. 1) is that of a salt, $C_{16}H_{38}N_4^{2+} \cdot 2C_{10}H_7COO^- \cdot 2C_2H_5OH$, in which the fully ordered cation lies across a centre of inversion, chosen for the sake of convenience as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while the anion and the ethanol molecule lie in general positions.



The cation adopts the usual and characteristic *trans*-III configuration (Barefield *et al.*, 1986), with four methyl groups in equatorial sites and two in axial sites, and with paired intracation N—H···N hydrogen bonds generating an $R_2^2(10)$ motif (Bernstein *et al.*, 1995). There is almost perfect staggering about all of the C—C and C—N bonds in the cation (Table 1), and there are four axial N—H bonds available for intermolecular hydrogen-bond formation, two on each face of the disc-like cation. The C—N bond lengths in the cation (Table 1) are consistent with the site of N-protonation, while the C—C distances in the anion exhibit the marked bond fixation typical of the naphthalene ring system.

Within the selected asymmetric unit, atoms N1 at (x, y, z) and N4 at $(1-x, 1-y, 1-z)$, both part of the cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, act as hydrogen-bond donors to, respectively, carboxylate atoms O1 and O2 in the anion at (x, y, z) , forming an $R_3^3(8)$ motif, while ethanol atom O3 also acts as a donor towards O2 (Fig. 1). In this manner, a centrosymmetric five-component aggregate is formed, which accommodates all of the hard (Desiraju & Steiner, 1999) hydrogen-bond donors. Similar $R_3^3(8)$ motifs involving $[(\text{tet-a})H_2]^{2+}$ cations and aromatic carboxylate anions have been observed in salts with terephthalate (Lough *et al.*, 2000), 5-hydroxyisophthalate (Burchell *et al.*, 2000) and 5-nitroisophthalate (MacLean *et al.*, 2002), although not in the analogous salts formed by 3- and

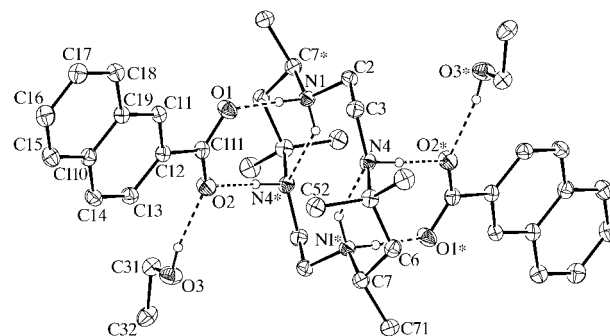


Figure 1

The centrosymmetric five-component aggregate in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and, for the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

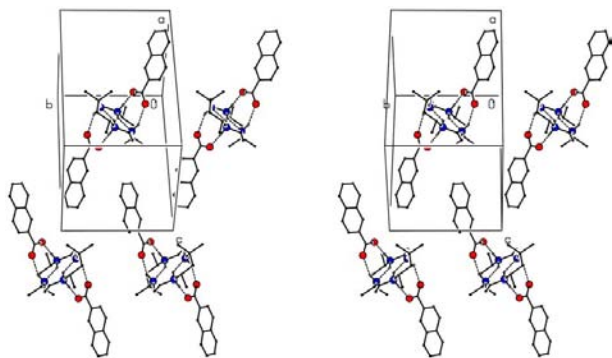


Figure 2

A stereoview of part of the crystal structure of (I), showing the near orthogonality of adjacent naphthalene rings. For the sake of clarity, the ethanol molecules and H atoms bonded to C atoms have been omitted.

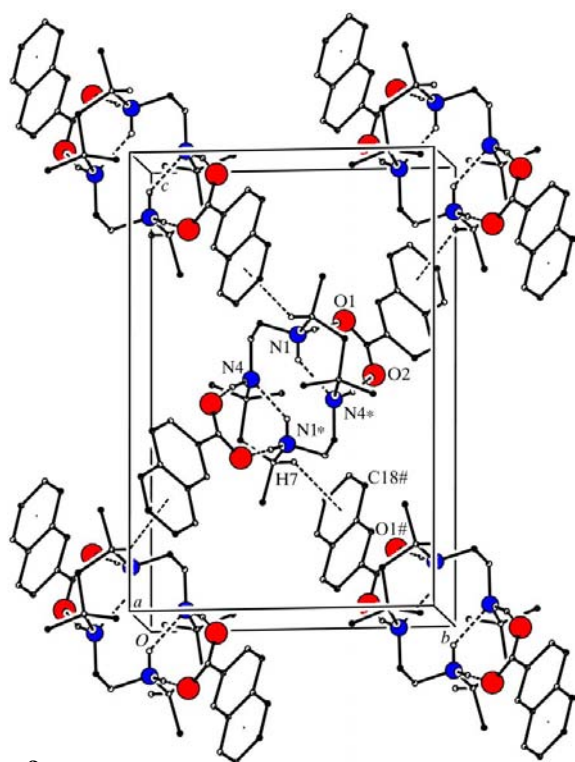


Figure 3

Part of the crystal structure of (I), showing the linking of the five-component aggregates into a (100) sheet by means of a C—H... π (arene) hydrogen bond. For the sake of clarity, the ethanol molecules and H atoms bonded to C atoms in the anion have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1-x, 1-y, 1-z)$ and $(x, \frac{3}{2}-y, z-\frac{1}{2})$, respectively.

4-hydroxybenzoate or 3,5-dihydroxybenzoate anions (Gregson *et al.*, 2000).

For the closest approach of naphthalene rings in adjacent aggregates in (I), the centroid separation is 5.493 (2) Å. Whereas in $[(C_{10}H_7COO)_2Ni(\text{cyclam})]$, the nearest-neighbour naphthoate units are related by inversion, in (I), they are related by a twofold screw axis, and the naphthalene rings involved are almost orthogonal (Fig. 2), with a dihedral angle of 84.5 (3)° between the ring planes, so that aromatic π - π -stacking interactions are absent. However, the aggregates are linked into sheets by a single C—H... π (arene) hydrogen bond

(Table 2). The metrical systematics of C—H... π (arene) hydrogen bonds have been studied by Braga *et al.* (1998) using neutron diffraction results extracted from the Cambridge Structural Database (April 1997 release; Allen, 2002). The most frequently observed H...Cg distances (Cg represents the centroid of the arene ring) lie in the range 2.9–3.0 Å, while the mean values of the C—H...Cg angles and C...Cg distances were found to be 142 (2)° and 3.69 (2) Å, respectively. The values found here for (I) are thus fairly typical for interactions of this type.

Atom C7 in the cation is adjacent to a protonated ring N atom, and hence the axial C7—H7 bond can be expected to be moderately acidic for an aliphatic C—H bond. Atom C7 at (x, y, z) , which lies in the cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as a hydrogen-bond donor to the unsubstituted C15–C110 aryl ring of the anion at $(x, \frac{3}{2}-y, z-\frac{1}{2})$, which forms part of the aggregate centred at $(\frac{1}{2}, 1, 0)$, while atom C7 at $(1-x, 1-y, 1-z)$ in the same $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ aggregate acts as a donor to the naphthoate anion at $(1-x, y-\frac{1}{2}, \frac{3}{2}-z)$, which is part of the aggregate centred at $(\frac{1}{2}, 0, 1)$. The two naphthoate anions in the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ aggregate likewise act as acceptors from atoms C7 in the aggregates centred at $(\frac{1}{2}, 0, 0)$ and $(\frac{1}{2}, 1, 1)$, and in this manner the five-component aggregates are linked into a (100) sheet (Fig. 3).

Experimental

Equimolar quantities of tet-a (Hay *et al.*, 1975) and 2-naphthoic acid were separately dissolved in ethanol. The solutions were mixed and the mixture was set aside to crystallize, producing analytically pure (I). Analysis, found: C 69.9, H 8.9, N 8.1%; $C_{42}H_{64}N_4O_6$ requires: C 70.0, H 9.0, N 7.8%. Crystals of (I) suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_{16}H_{38}N_4^{2+} \cdot 2C_{11}H_7O_2^- \cdot 2C_2H_6O$
 $M_r = 720.97$
 Monoclinic, $P2_1/c$
 $a = 10.9563$ (4) Å
 $b = 10.9584$ (5) Å
 $c = 17.1665$ (8) Å
 $\beta = 101.446$ (2)°
 $V = 2020.08$ (15) Å³
 $Z = 2$

$D_x = 1.185$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4606 reflections
 $\theta = 2.8$ – 27.5°
 $\mu = 0.08$ mm⁻¹
 $T = 150$ (1) K
 Block, colourless
 $0.32 \times 0.25 \times 0.20$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offsets
 17 192 measured reflections
 4606 independent reflections
 3130 reflections with $I > 2\sigma(I)$

$R_{int} = 0.075$
 $\theta_{max} = 27.5^\circ$
 $h = -14 \rightarrow 13$
 $k = -14 \rightarrow 14$
 $l = -22 \rightarrow 22$

Table 1

Selected geometric parameters (Å, °).

N1—C2	1.487 (2)	N4—C3	1.465 (2)
N1—C7 ⁱ	1.501 (2)	N4—C5	1.495 (2)
N1—C2—C3—N4	62.09 (16)	C5—C6—C7—N1 ⁱ	56.87 (17)
C2—C3—N4—C5	−174.22 (13)	C6—C7—N1 ⁱ —C2 ⁱ	−163.05 (12)
C3—N4—C5—C6	−170.12 (13)	C7 ⁱ —N1—C2—C3	172.03 (12)
N4—C5—C6—C7	−69.22 (17)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

Cg2 is the centroid of the C15–C110 ring of the anion.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1B···N4 ⁱ	0.92	2.04	2.791 (2)	138
N1—H1A···O1	0.92	1.70	2.624 (2)	178
N4—H4···O2 ⁱ	0.92	2.30	3.136 (2)	151
O3—H3···O2	0.84	1.90	2.728 (2)	171
C7—H7···Cg2 ⁱⁱ	1.00	2.94	3.785 (2)	143

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, \frac{3}{2}-y, z-\frac{1}{2}$.**Refinement**Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.048$ $wR(F^2) = 0.130$ $S = 1.02$

4606 reflections

241 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.3194P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.16 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 1997)

Extinction coefficient: 0.014 (3)

The space group $P2_1/c$ was uniquely assigned from the systematic absences. H atoms were treated as riding, with O—H distances of 0.84 Å, N—H distances of 0.92 Å, and C—H distances of 0.95 (aromatic), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic CH).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC, Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1618). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- 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.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Braga, D., Grepioni, F. & Tedesco, E. (1998). *Organometallics*, **17**, 2669–2672.
- Burchell, C. J., Ferguson, G., Lough, A. J. & Glidewell, C. (2000). *Acta Cryst.* **B56**, 1054–1062.
- Desiraju, G. R. & Steiner, T. (1999). Editors. *The Weak Hydrogen Bond*, pp. 86–89. Oxford University Press.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst.* **B56**, 39–57.
- Hay, R. W., Lawrance, G. A. & Curtis, N. F. (1975). *J. Chem. Soc. Perkin Trans.* **1**, pp. 591–593.
- Lough, A. J., Gregson, R. M., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* **B56**, 85–93.
- MacLean, E. J., Teat, S. J., Farrell, D. M. M., Ferguson, G. & Glidewell, C. (2002). *Acta Cryst.* **C58**, o470–o473.
- Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2002). *PLATON*. Version of June 2002. University of Utrecht, The Netherlands.
- Zakaria, C. M., Ferguson, G., Lough, A. J. & Glidewell, C. (2002). *Acta Cryst.* **B58**, 78–9.