Acta Cryst. (1996). C**52**, 1128–1131

Bis(μ-4-hydroxybenzoato-*O*:*O*′)-bis[(*N*,*N*-diethylnicotinamide-*N*^{1})-(4-hydroxybenzoato-*O*)zinc(II)] Dihydrate

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(*Received 7 August 1995; accepted 27 November 1995*)

Abstract

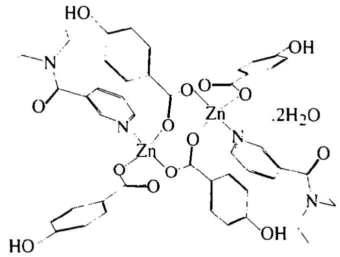
The binuclear centrosymmetric zinc complex of the title compound, $[Zn_2(C_7H_5O_3)_4(C_{10}H_{14}N_2O)_2].2H_2O$, contains four benzoate ligands, two of which bridge the two Zn atoms [Zn···Zn′ 6.685 (5) Å] and two of which coordinate as monodentate ligands. Each Zn atom is coordinated by three O atoms and an N atom from an *N*,*N*-diethylnicotinamide ligand with slightly distorted tetrahedral coordination geometry. The water molecules are hydrogen bonded to the nicotinamide O atoms [O···O 2.756 (4) Å].

Comment

The solid-state structures of anhydrous zinc(II) carboxylates include one-dimensional (Guseinov, Musaev, Usubaliev, Amiraslanov & Mamedov, 1984; Clegg, Little & Straughan, 1986*a*), two-dimensional (Clegg, Little & Straughan, 1986*b*, 1987) and three-dimensional (Capilla & Aranda, 1979) polymeric motifs of different types, while discrete monomeric complexes with octahedral or tetrahedral coordination geometry are found if water or other donor molecules are coordinated to Zn (van Niekerk, Schoening & Talbot, 1953; Usubaliev, Guliev, Musaev, Ganbarov, Ashurova & Movsumov, 1992). In hexaaquazinc(II) bis(4-hydroxybenzoate) dihydrate, $[Zn(H_2O)_6](4\text{-}HOC_6H_4COO)_2.2H_2O$, which is isostructural with the corresponding Mg^{II}, Co^{II}, Ni^{II} and Mn^{II} compounds, the carboxylate ion lies out of the coordination sphere of the Zn atom (Musaev, Nadzhafov & Mamedov, 1983), while $Zn(4\text{-}HOC_6H_4COO)_2.4(C_5H_5N)$ forms a clathrate consisting of $[Zn(4\text{-}HOC_6H_4COO)_2(C_5H_5N)_2]$ units with tetrahedral coordination geometry and free pyridine molecules (Nadzhafov, Usubaliev, Amiraslanov, Movsumov & Mamedov, 1981). Clegg, Little & Straughan (1986*c*) have reported a series of air-stable binuclear zinc(II) complexes, $[Zn_2(\text{carboxylate})_4(\text{base})_2]$. There are also structural reports of polymeric zinc(II) carboxylates which contain binuclear units such as $[Zn_2(MeCOO)_3]^+$ (Birnbaum, Cotton, Dori & Kapon, 1984) and $[Zn_2(\text{crotonate})_3]^+$ (Clegg, Little & Straughan, 1986*a*).

N,*N*-Diethylnicotinamide (DENA) is an important respiratory stimulant. The structures of several complexes obtained by reacting divalent transition metal ions with DENA have been determined, including those of $Zn(DENA)_2(NCS)_2(H_2O)_2$ (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1973*b*), $Mn(DENA)_2(NCS)_2$ (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1973*a*), $Cd(DENA)(SCN)_2$ (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1972) and $Cu_2(DENA)_2(C_6H_5COO)_4$ (Hökelek, Necefoğlu & Balcı, 1995). DENA acts as a bidentate ligand in $Mn(DENA)_2(NCS)_2$, while in $Cd(DENA)(SCN)_2$, $Zn(DENA)_2(NCS)_2(H_2O)_2$ and $Cu_2(DENA)_2(C_6H_5COO)_4$, DENA is monodentate. In $Cu_2(DENA)_2(C_6H_5COO)_4$, the benzoate ion acts as a bidentate ligand.

The determination of the structure of the title compound, (I), was undertaken in order to define the properties of DENA and the 4-hydroxybenzoate ligand, and to compare the results obtained here with those reported previously.



(I)

The title compound contains a binuclear Zn^{II} complex in which there are two DENA and four 4-hydroxybenzoate ligands. Two benzoate ions act as monodentate ligands and two act as bidentate ligands, bridging the two Zn atoms. The DENA ligands are monodentate and coordinate through the pyridine N atom (which is more basic than the O atom). The two water molecules in the compound do not act as ligands, but are incorporated into the crystal lattice by hydrogen bonds. A view of the molecule and the atomic numbering scheme used is given in Fig. 1.

The structure of the title compound is different from the structures of the binuclear complexes $[M_2(\text{carboxylate})_4(\text{donor})_2]$ (M = Zn^{II} or Cu^{II}) where two donors are coordinated in axial positions and four carboxylate ions bridge the two M^{II} ions in *syn–syn* fashion (Clegg, Little & Straughan, 1986*c*; Hökelek, Necefoğlu & Balcı, 1995). In (I), two *p*-hydroxybenzoate ligands bridge in a *syn–anti* arrangement. The valence angles around Zn [98.4 (1)–115.7 (1)°] show that Zn has distorted tetrahedral coordination geometry. In the binuclear complex $Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N_2)_2$ (Clegg, Little & Straughan, 1986*c*), the average Zn—O bond

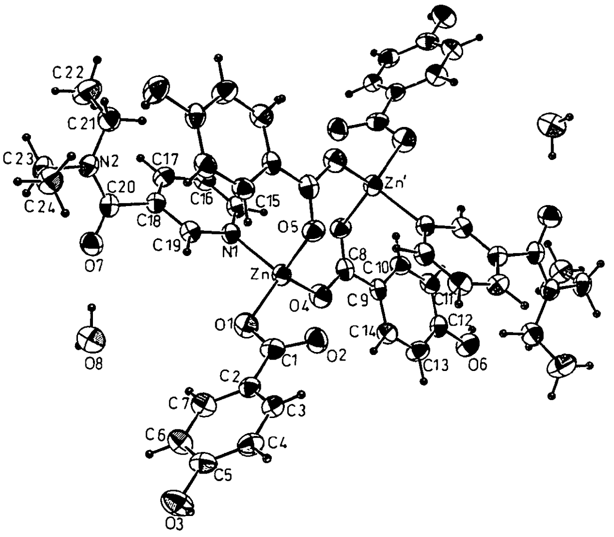


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

length [2.043 (2) Å] is longer than the corresponding value in (I) [1.953 (2) Å], but Zn is five-coordinate. The length of the bond between the Zn atom and the N heteroatom of the DENA molecule [Zn—N1 2.049 (2) Å] is in good agreement with the values reported for other tetrahedrally coordinated Zn complexes [2.006 (5) Å in $Zn_2(DENA)_2(NCS)_4$ (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1973*c*), 2.054 (6) and 2.055 (6) Å in $ZnCl_2(DENA)_2$ (Khodashova, Poray-Koshits, Rubinchik, Butman & Tsintsadze, 1978) and 2.068 (7) Å in $ZnI_2(DENA)_2$ (Sergienko, Poray-Koshits, Rubinchik, Butman & Tsintsadze, 1978)] while it is shorter than the corresponding Zn—N bond length in the octahedrally coordinated zinc complex $Zn(DENA)_2(NCS)_2.2(H_2O)$ [2.171 (4) Å (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1973*b*)].

The Zn···Zn' distance in the title compound [6.685 (5) Å] is much longer than the values reported in the other binuclear complexes {2.976 Å in $[Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$ (Clegg, Little & Straughan, 1986*c*), 3.538 Å in $[Zn_2(MeCOO)_3]$ (Birnbaum, Cotton, Dori & Kapon, 1984), 3.27 Å in $[Zn(C_6H_5COO)_2]$ (Guseinov, Musaev, Usubaliev, Amiraslanov & Mamedov, 1984) and 3.247 (3) Å in zinc(II) crotonate (Clegg, Little & Straughan, 1986*a*)}. The bond lengths and angles in the DENA molecule and the phenyl rings of the monodentate and bidentate *p*-hydroxybenzoate anions are in good agreement with the values reported in the literature (Nadzhafov, Usubaliev, Amiraslanov, Movsumov & Mamedov, 1981; Hökelek, Necefoğlu & Balcı, 1995). The aromatic bonds C5—O3 and C12—O6 have bond lengths of 1.360 (4) and 1.355 (4) Å, respectively, and are in agreement with the corresponding values for 4-hydroxybenzoic acid monohydrate (Colapietro, Domenicano & Marciante, 1979). The pyridine ring and the O7—C20—N2 plane form a dihedral angle of 129.7 (2)°. The dihedral angles between the carboxy groups O1—C1—O2 and O4—C8—O5 and the least-squares planes through the phenyl rings C2–C7 and C9–C14 are 17.9 (7) and 136.1 (2)°, respectively.

Experimental

The title compound was prepared by the reaction of 0.0030 mol of $Zn(4\text{-}HO\text{-}C_6H_5COO)_2.8H_2O$ and 0.0056 mol of DENA in 80 ml of H_2O. The mixture was filtered and set aside for crystallization at ambient temperature for one day.

Crystal data

$[Zn_2(C_7H_5O_3)_4(C_{10}H_{14}\text{-}N_2O)_2].2H_2O$
$M_r = 1071.7$
Monoclinic
$P2_1/c$
$a = 8.681$ (3) Å
$b = 11.772$ (2) Å
$c = 23.730$ (6) Å
$\beta = 95.8$ (2)°
$V = 2413.1$ (11) Å^3
$Z = 2$
$D_x = 1.476$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 5$–11°
$\mu = 1.09$ mm^{-1}
$T = 298$ K
Plate
0.60 × 0.52 × 0.12 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5365 measured reflections
3847 independent reflections
2852 observed reflections [$I > 3\sigma(I)$]
$R_{\text{int}} = 0.017$

$\theta_{\text{max}} = 24°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = -26 \rightarrow 26$
3 standard reflections monitored every 250 reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.0328$
$wR = 0.0396$
$S = 1.34$
2852 reflections
420 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\text{max}} = 0.10$
$\Delta\rho_{\text{max}} = 0.345$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.605$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\text{eq}} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Zn	0.36177 (4)	0.06799 (3)	0.05011 (1)	2.602 (6)
N1	0.1817 (3)	0.0736 (2)	−0.0128 (1)	2.52 (5)
N2	−0.1521 (3)	0.3479 (2)	−0.1055 (1)	2.76 (5)

O1	0.2807 (3)	0.1607 (2)	0.10834 (9)	3.80 (5)
O2	0.5284 (3)	0.1619 (2)	0.14004 (9)	3.71 (5)
O3	0.2523 (3)	0.5185 (2)	0.30551 (9)	4.33 (5)
O4	0.4215 (3)	−0.0834 (2)	0.07620 (9)	3.43 (5)
O5	0.5220 (2)	0.1399 (2)	0.00883 (8)	3.12 (5)
O6	0.7734 (3)	−0.5312 (2)	0.1541 (1)	3.85 (5)
O7	−0.1765 (3)	0.3103 (2)	−0.01362 (9)	3.74 (5)
O8	−0.2121 (3)	0.2753 (2)	0.0992 (1)	4.25 (5)
C1	0.3931 (4)	0.1955 (3)	0.1431 (1)	2.95 (7)
C2	0.3569 (4)	0.2798 (3)	0.1865 (1)	2.68 (6)
C3	0.4733 (4)	0.3457 (3)	0.2141 (1)	2.98 (7)
C4	0.4421 (4)	0.4275 (3)	0.2533 (1)	3.22 (7)
C5	0.2914 (4)	0.4428 (3)	0.2661 (1)	3.15 (7)
C6	0.1726 (4)	0.3777 (3)	0.2390 (1)	3.44 (7)
C7	0.2052 (4)	0.2979 (3)	0.1994 (1)	3.26 (7)
C8	0.4809 (4)	−0.1549 (3)	0.0441 (1)	2.71 (6)
C9	0.5541 (3)	−0.2567 (2)	0.0718 (1)	2.48 (6)
C10	0.6023 (4)	−0.3479 (3)	0.0401 (1)	2.92 (7)
C11	0.6738 (4)	−0.4404 (3)	0.0664 (1)	3.03 (6)
C12	0.7000 (4)	−0.4443 (3)	0.1252 (1)	2.90 (6)
C13	0.6521 (4)	−0.3545 (3)	0.1568 (1)	3.47 (7)
C14	0.5796 (4)	−0.2628 (3)	0.1299 (1)	3.11 (7)
C15	0.1564 (4)	−0.0086 (3)	−0.0521 (1)	2.82 (6)
C16	0.0397 (4)	−0.0031 (3)	−0.0949 (1)	3.14 (7)
C17	−0.0546 (4)	0.0912 (3)	−0.0995 (1)	2.93 (7)
C18	−0.0284 (3)	0.1787 (2)	−0.0603 (1)	2.49 (6)
C19	0.0884 (4)	0.1651 (2)	−0.0173 (1)	2.64 (6)
C20	−0.1262 (3)	0.2842 (3)	−0.0586 (1)	2.74 (6)
C21	−0.0853 (4)	0.3301 (3)	−0.1589 (1)	3.64 (7)
C22	−0.1999 (5)	0.2836 (4)	−0.2054 (2)	5.00 (9)
C23	−0.2401 (4)	0.4543 (3)	−0.1012 (1)	3.31 (7)
C24	−0.1383 (4)	0.5488 (3)	−0.0753 (2)	3.85 (8)

Table 2. *Selected geometric parameters (Å, °)*

Zn—N1	2.049 (2)	C3—C4	1.386 (5)
Zn—O1	1.948 (2)	C4—C5	1.381 (5)
Zn—O4	1.941 (2)	C5—C6	1.388 (5)
Zn—O5	1.970 (2)	C6—C7	1.378 (5)
N1—C15	1.348 (4)	C8—C9	1.479 (4)
N1—C19	1.345 (4)	C9—C10	1.399 (4)
N2—C20	1.343 (4)	C9—C14	1.378 (4)
N2—C21	1.460 (4)	C10—C11	1.374 (4)
N2—C23	1.476 (4)	C11—C12	1.394 (4)
O1—C1	1.279 (4)	C12—C13	1.384 (5)
O2—C1	1.246 (4)	C13—C14	1.374 (5)
O3—C5	1.360 (4)	C15—C16	1.362 (4)
O4—C8	1.278 (4)	C16—C17	1.377 (4)
O6—C12	1.355 (4)	C17—C18	1.392 (4)
O7—C20	1.232 (4)	C18—C19	1.373 (4)
C1—C2	1.487 (4)	C18—C20	1.508 (4)
C2—C3	1.383 (4)	C21—C22	1.512 (5)
C2—C7	1.395 (5)	C23—C24	1.512 (5)
N1—Zn—O1	101.3 (1)	O3—C5—C4	122.9 (3)
N1—Zn—O4	114.92 (9)	O3—C5—C6	117.2 (3)
N1—Zn—O5	98.41 (9)	C4—C5—C6	119.9 (3)
O1—Zn—O4	113.11 (9)	C5—C6—C7	120.0 (3)
O1—Zn—O5	115.74 (9)	C2—C7—C6	121.0 (3)
O4—Zn—O5	112.07 (9)	O4—C8—C9	116.8 (3)
Zn—N1—C15	122.7 (2)	C8—C9—C10	121.4 (3)
Zn—N1—C19	119.4 (2)	C8—C9—C14	120.3 (3)
C15—N1—C19	117.8 (2)	C10—C9—C14	118.2 (3)
C20—N2—C21	126.3 (3)	C9—C10—C11	120.7 (3)
C20—N2—C23	117.5 (3)	C10—C11—C12	120.1 (3)
C21—N2—C23	115.7 (2)	O6—C12—C11	123.5 (3)
Zn—O1—C1	109.5 (2)	O6—C12—C13	117.1 (3)
Zn—O4—C8	121.8 (2)	C11—C12—C13	119.4 (3)
O1—C1—O2	121.3 (3)	C12—C13—C14	119.9 (3)
O1—C1—C2	117.5 (3)	C9—C14—C13	121.7 (3)
O2—C1—C2	121.2 (3)	N1—C15—C16	122.7 (3)
C1—C2—C3	120.6 (3)	C15—C16—C17	119.2 (3)
C1—C2—C7	121.5 (3)	C16—C17—C18	119.3 (3)
C3—C2—C7	117.9 (3)	C17—C18—C19	118.1 (3)
C2—C3—C4	121.7 (3)	C17—C18—C20	125.1 (3)
C3—C4—C5	119.4 (3)	C19—C18—C20	116.7 (3)
N1—C19—C18	122.9 (3)	O7—C20—C18	118.6 (3)
N2—C20—O7	122.3 (3)	N2—C21—C22	113.4 (3)
N2—C20—C18	119.1 (3)	N2—C23—C24	111.7 (3)
O1—Zn—N1—C15	−154.3 (2)	O1—Zn—N1—C19	29.1 (2)
O4—Zn—N1—C15	−32.0 (3)	O4—Zn—N1—C19	151.4 (2)
O5—Zn—N1—C15	87.2 (2)	O5—Zn—N1—C19	−89.4 (2)
N1—Zn—O1—C1	−160.0 (2)	O4—Zn—O1—C1	76.5 (2)
O5—Zn—O1—C1	−54.8 (2)	N1—Zn—O4—C8	66.1 (3)
O5—Zn—O4—C8	−45.1 (3)	C21—N2—C20—C18	−4.6 (5)
C20—N2—C21—C22	106.6 (4)	C23—N2—C21—C22	−81.7 (4)
C20—N2—C23—C24	80.3 (3)	Zn—O1—C1—O2	6.2 (4)
Zn—O1—C1—C2	172.4 (2)	O1—C1—C2—C3	−160.7 (3)
O1—C1—C2—C7	17.0 (4)	O2—C1—C2—C3	17.8 (4)
O2—C1—C2—C7	−164.5 (3)	O4—C8—C9—C10	170.6 (3)
C17—C18—C20—N2	−53.8 (4)	C17—C18—C20—O7	127.9 (3)
C19—C18—C20—N2	131.1 (3)	C19—C18—C20—O7	−47.2 (4)

The structure was solved by direct methods. H atoms were located from a difference map and were refined isotropically.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of a CAD-4 diffractometer under grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey. The authors are also grateful to Dr Zeynel Kılıç of the Department of Chemistry, Ankara University, and Dr Metin Balcı of the Department of Chemistry, Atatürk University, for helpful discussions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1306). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1131–1134

Copper and Manganese Sulfanilate Hydrates

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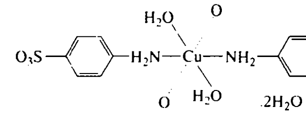
(*Received 23 August 1995; accepted 6 November 1995*)

Abstract

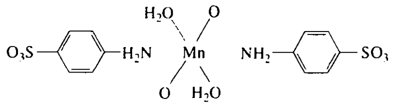
The title compounds, bis(4-aminobenzenesulfonato)-diaquacopper(II) dihydrate, $[Cu(C_6H_6NO_3S)_2(H_2O)_2].2H_2O$, and bis(4-aminobenzenesulfonato)diaquamanganese(II), $[Mn(C_6H_6NO_3S)_2(H_2O)_2]$, have structures in which the sulfanilate anions are arranged in layers with the functional groups directed towards adjacent layers. Between these slabs are the metal cations and water molecules. The Cu atom sits in a tetragonally distorted octahedron, with short contacts to two amine N atoms and two water molecules. Two sulfonate O atoms provide the longer interactions. The other water molecules are anchored by hydrogen bonds to the sulfonate groups. The Mn atom also displays a tetragonal distortion of its octahedral coordination to two sulfonate O atoms, two water molecules and, at the elongated vertices, two amine N atoms. The manganese salt contains no free water molecules. Both structures differ from those of the reported cobalt and zinc salts.

Comment

The copper and manganese sulfanilate salts, (I) and (II), respectively, were prepared as part of a continuing study of the coordination chemistry and layering patterns of functionalized sulfonic acids (Gunderman & Squattrito, 1995).



(I)



(II)

As shown in Fig. 1, the Cu cation, which rests on a center of inversion, is coordinated to the amine N atoms of two sulfanilate anions and to two water molecules in a square-planar arrangement. Two O atoms from the sulfonate groups of other anions are at the remaining vertices of the octahedron, approximately 0.4 Å further away. Thus, the copper coordination shows a classic Jahn–Teller distortion similar to many reported examples (Melnik, 1982). The packing diagram (Fig. 2) shows that the sulfanilate anions occur in layers that stack along the *b* axis. Neighboring anions in a layer have the polar groups oriented towards opposite faces of the layer. In addition, they are canted slightly with respect to each other and the rings are approximately 16° out of parallel. This type of anion packing arrangement is also observed in sodium sulfanilate dihydrate (Bats, 1977). The layers are held together by the Cu cations, each of which is bonded to four different anions, two from each adjacent layer. The structure is further reinforced by hydrogen bonds (Table 3) involving the amine group, both water molecules and the sulfonate group. This structure is quite similar to that of the cobalt (Shakeri & Haussuhl, 1992*a*) and zinc (Shakeri & Haussuhl, 1992*b*) sulfanilate tetrahydrates, but is distinguished by the distorted coordination of the Cu atom. In contrast, the octahedral environments of the cobalt (Co—*L* 2.06–2.19 Å) and zinc (Zn—*L* 2.09–2.18 Å) atoms are far more regular.

The manganese compound is a dihydrate, with all water molecules directly coordinated to the metal ion. The Mn cation (Fig. 3) also sits on an inversion center and coordinates to two amine N atoms, two water molecules and two sulfonate O atoms. The octahedron about Mn is distorted as the Mn—N distances are longer than the four Mn—O distances. Similar distortions have been observed in other mixed-ligand Mn^{II} complexes (Stephens, 1977), though the elongated contacts are often *cis* rather than *trans*. The packing pattern of the anions also differs from that found in the tetrahydrates. Here again, neighboring anions have the amine and sulfonate groups flipped, but they are not tilted with respect