Acta Cryst. (1995). C**51**, 1252–1254

Sodium Cyclododecylphosphonic Acid Monoethyl Ester Trihydrate

RAINER RUDERT

Bundesanstalt für Materialforschung und -prüfung, Rudower Chaussee 5, 12489 Berlin, Germany

GUNTHER CZICHOCKI, BERND WEILAND AND DIETER VOLLHARDT

Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5, 12489 Berlin, Germany

(*Received* 27 *October* 1994; *accepted* 9 *January* 1995)

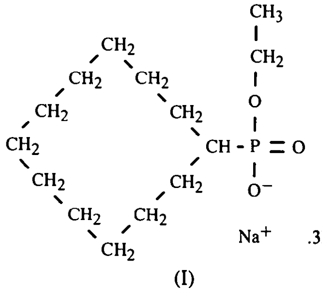
Abstract

The conformation of the cyclododecyl ring in the title compound, $Na^+.C_{14}H_{28}O_3P^-.3H_2O$, has slightly distorted 422 symmetry. The molecules are packed in a head-to-head arrangement. The hydrophilic parts of neighbouring molecular layers are connected *via* coordination to Na^+ and hydrogen bonds.

Comment

Knowledge of the structural relationships of three-dimensional crystals to their two-dimensional adsorption layers leads to an understanding of the molecular arrangements on interfaces. However, no systematic information is available on the structural effect of the hydrophilic head group or the counterion of anionic amphiphiles.

The molecular structure of the title compound, sodium cyclododecylphosphonic acid monoethyl ester trihydrate, (I), is very similar to that of sodium cyclododecyl sulfate trihydrate (Rudert, Vollhardt & Czichocki, 1994). The amphiphilic nature of this sulfate was modified by exchange of the polar head group, *i.e.* the sulfate group was formally substituted by a phosphonic acid monoethyl ester group (sodium salt). Both compounds have an identical hydrophobic moiety and contain one Na^+ cation in the hydrophilic part of the molecule.



(I)

The ring conformation of the title compound is the same as that of the sulfate compound and the average deviation of the C atoms from an ideal dodecyl ring, which has 422 (D_4) symmetry, is 0.047 Å. This deviation is less than in the sulfate compound, so it is clear that the ring symmetry is less distorted by a phosphonate group than by a sulfate group.

The average C—C bond distance is 1.521 Å and the average C—C—C bond angle is 114.7°, which coincidentally are exactly the same values as for the sulfate compound.

The torsion angles within the head group are completely different from the corresponding angles in 1-hydroxyphosphonic acid monoethyl ester (Hammerschmidt & Völlenkle, 1986), which is a result of the free rotation about the P—O3 and O3—C31 bonds. As in 1-hydroxyphosphonic acid monoethyl ester, the P—O_{ester} distance is longer than the other two P—O distances. The P—O1 and P—O2 bonds must, therefore, both have partial double-bond character and the negative charge of the phosphonate group must be on atoms O1 and O2. The elongated shape of the displacement ellipsoid of O3 indicates some disorder at this position.

The molecules are arranged in double layers in a head-to-head arrangement. The area per molecule within each layer is 42.13 (1) Å^2, which is nearly the same as in the sulfate compound. In the title compound, all ring planes are parallel (Fig. 2), whereas in the sulfate compound the ring planes of neighbouring layers are perpendicular. There are 11 short (< 4.2 Å) C···C contacts between rings and five C···C contacts between the ethyl group and the ring atoms.

The Na^+ cations are situated at two different positions on a twofold axis, *i.e.* Na1 and Na2. Each is sixfold coordinated by O atoms forming distorted octahedra. Na1 coordinates exclusively with water O atoms, while Na2 coordinates with four water O atoms and two O1 atoms of the phosphonic group. O1···Na2···O1

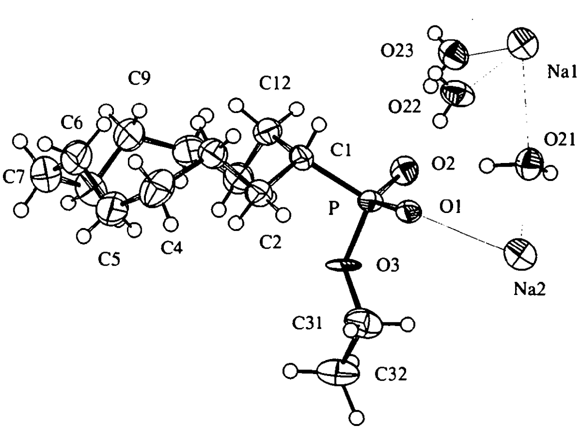


Fig. 1. *PLATON* (Spek, 1990) drawing of the asymmetric unit of the title compound. The displacement ellipsoids are drawn at the 50% probability level. Thin lines indicate the $Na^+\cdots O$ contacts.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995

contacts connect two molecular layers in the crystal. There are several hydrogen bonds between water molecules, and also between water molecules and atoms O1 and O2 of the phosphonate group (Table 2 and Fig. 3).

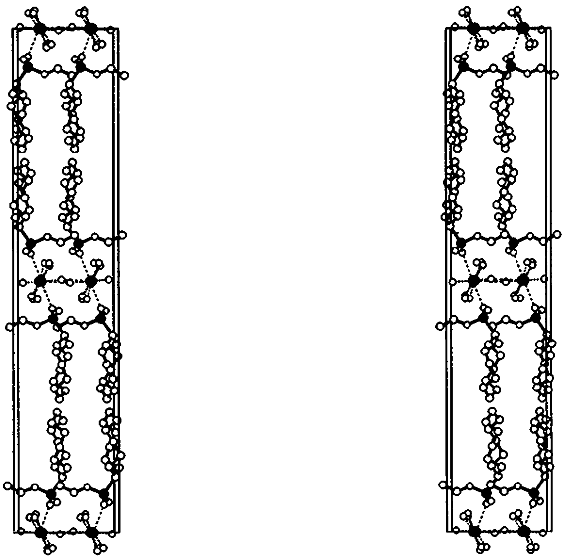


Fig. 2. *SCHAKAL*92 (Keller, 1992) drawing of the molecular packing viewed along the [010] direction. The $Na^+\cdots O$ contacts are symbolized by dotted lines and H atoms have been omitted.

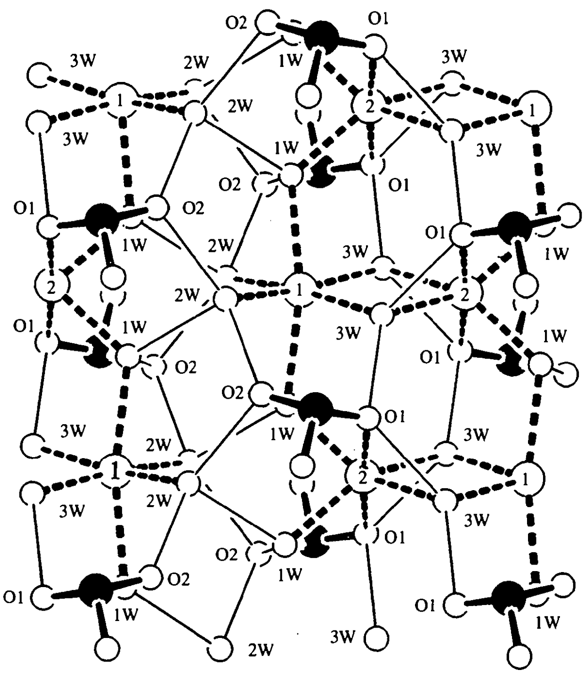


Fig. 3. *SCHAKAL*92 (Keller, 1992) stereodrawing of the intermolecular contacts within the polar region viewed along the [100] direction. Filled circles are P atoms, circles with numbers inside are Na^+ cations, all other open circles are O atoms, dotted lines indicate $Na^+\cdots O$ contacts, thin lines are $O\cdots O$ hydrogen bridges, and labels 1*W*, 2*W* and 3*W* correspond to O21, O22 and O23, respectively.

Experimental

Cyclododecylphosphonic acid diethyl ester was prepared by the reaction of cyclododecene (Merck synthesis grade) with diethyl phosphite using dicumyl peroxide as catalyst (1 mol %) at 448–453 K. The diester was purified by distillation (semimicro Spaltrohr column) and the purity was checked by gas–liquid chromatography. It was then saponified with alcoholic sodium hydroxide, by heating under reflux, to yield the title compound, which was recrystallized several times from alcohol/chloroform and chloroform and characterized by both elemental analysis and ^{13}C NMR spectroscopy.

Crystal data

$Na^+.C_{14}H_{28}O_3P^-.3H_2O$
$M_r = 352.39$
Orthorhombic
Pbcn
$a = 43.851\ (8)$ Å
$b = 9.588\ (1)$ Å
$c = 8.788\ (2)$ Å
$V = 3694\ (1)$ Å^3
$Z = 8$
$D_x = 1.27$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 16–19°$
$\mu = 1.734$ mm^{-1}
$T = 299$ K
Prism
0.62 × 0.30 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: numerical
$T_{min} = 0.4746$, $T_{max} = 0.8962$
2801 measured reflections
1770 independent reflections

1504 observed reflections $[I > 1.5\sigma(I)]$
$R_{int} = 0.084$
$\theta_{max} = 47.98°$
$h = -1 \rightarrow 42$
$k = 0 \rightarrow 9$
$l = -8 \rightarrow 8$
3 standard reflections
frequency: 30 min
intensity decay: 1.68%

Refinement

Refinement on F
$R = 0.060$
$wR = 0.069$
$S = 2.518$
1504 reflections
227 parameters
H atoms of CH_2 groups kept fixed at calculated positions, all others taken from Fourier maps and refined with U fixed

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$
$(\Delta/\sigma)_{max} = 0.092$
$\Delta\rho_{max} = 0.289$ e Å^{-3}
$\Delta\rho_{min} = -0.465$ e Å^{-3}
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)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Na1	1	−0.2791 (2)	1/4	0.042 (2)
Na2	1	−0.1209 (3)	−1/4	0.043 (2)
O21	0.99710 (7)	−0.3065 (3)	−0.0574 (4)	0.042 (2)
O22	1.03039 (7)	−0.0811 (3)	0.1594 (4)	0.044 (2)
O23	1.03606 (6)	−0.4584 (3)	0.1893 (3)	0.046 (2)
P	1.07545 (3)	−0.2379 (1)	−0.1391 (1)	0.0292 (8)
O1	1.05532 (6)	−0.1115 (3)	−0.1422 (3)	0.031 (2)
O2	1.05985 (6)	−0.3687 (3)	−0.0869 (4)	0.037 (2)
O3	1.08912 (7)	−0.2671 (3)	−0.3048 (3)	0.038 (2)

C1	1.1091 (1)	−0.2060 (4)	−0.0257 (5)	0.032 (3)
C2	1.1292 (1)	−0.0909 (4)	−0.0942 (5)	0.038 (3)
C3	1.1512 (1)	−0.0235 (5)	0.0166 (6)	0.048 (3)
C4	1.1780 (1)	0.0503 (5)	−0.0582 (6)	0.060 (4)
C5	1.2013 (1)	−0.0471 (6)	−0.1264 (6)	0.060 (4)
C6	1.2198 (1)	−0.1306 (6)	−0.0142 (7)	0.063 (4)
C7	1.2363 (1)	−0.2577 (6)	−0.0795 (7)	0.067 (4)
C8	1.2151 (1)	−0.3716 (6)	−0.1360 (6)	0.064 (4)
C9	1.1966 (1)	−0.4431 (6)	−0.0134 (6)	0.061 (4)
C10	1.1675 (1)	−0.5146 (5)	−0.0670 (6)	0.054 (3)
C11	1.1425 (1)	−0.4138 (5)	−0.1157 (6)	0.044 (3)
C12	1.1272 (1)	−0.3380 (5)	0.0156 (6)	0.040 (3)
C31	1.0787 (1)	−0.2039 (5)	−0.4392 (6)	0.056 (4)
C32	1.0921 (1)	−0.2699 (5)	−0.5737 (6)	0.053 (4)

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

P—O1	1.500 (3)	C4—C5	1.510 (7)
P—O2	1.501 (3)	C5—C6	1.509 (8)
P—O3	1.598 (3)	C6—C7	1.528 (8)
P—C1	1.809 (5)	C7—C8	1.517 (8)
O3—C31	1.404 (6)	C8—C9	1.514 (8)
C1—C2	1.535 (6)	C9—C10	1.524 (7)
C1—C12	1.537 (6)	C10—C11	1.521 (7)
C2—C3	1.515 (7)	C11—C12	1.520 (7)
C3—C4	1.518 (7)	C31—C32	1.465 (8)
Na1···O21	2.718 (3)	Na2···O21	2.459 (3)
Na1···O22	2.453 (3)	Na2···O22^{i}	2.481 (3)
Na1···O23	2.395 (3)	Na2···O1	2.606 (3)
O1—P—O2	114.4 (2)	C2—C3—C4	114.4 (4)
O1—P—O3	110.2 (2)	C3—C4—C5	114.0 (4)
O1—P—C1	110.7 (2)	C4—C5—C6	115.7 (4)
O2—P—O3	107.7 (2)	C5—C6—C7	115.6 (5)
O2—P—C1	110.2 (2)	C6—C7—C8	114.0 (4)
O3—P—C1	103.0 (2)	C7—C8—C9	115.0 (5)
P—O3—C31	124.7 (3)	C8—C9—C10	115.7 (5)
P—C1—C2	112.0 (3)	C9—C10—C11	113.8 (4)
P—C1—C12	114.4 (3)	C10—C11—C12	114.0 (4)
C2—C1—C12	112.9 (4)	C1—C12—C11	116.2 (4)
C1—C2—C3	114.9 (4)	O3—C31—C32	111.3 (4)

Symmetry code: (i) $x, -y, z - \frac{1}{2}$.

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *PLATON*92 (Spek, 1990) and *SCHAKAL*92 (Keller, 1992). Software used to prepare material for publication: *MolEN BTABLE*, *PTABLE* and *CIF IN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, torsion angles and contact distances greater than 2.39Å, have been deposited with the IUCr (Reference: SE1077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Enraf–Nonius (1977). *CAD*-4 *Operations Manual*. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Hammerschmidt, F. & Völlenkle, H. (1986). *Liebigs Ann. Chem.* pp. 2053–2064.

Keller, E. (1992). *SCHAKAL92. Computer Program for the Graphic Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.

Rudert, R., Vollhardt, D. & Czichocki, G. (1994). *Acta Cryst.* **C50**, 1054–1057.

Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.

Acta Cryst. (1995). **C51**, 1254–1258

Two Anionic Indium(III)–Thiocyanate Complexes with Potassium-Centred Complex Cations

CLAIRE J. CARMALT, WILLIAM CLEGG,*
MARK R. J. ELSEGOOD, BORIS O. KNEISEL AND
NICHOLAS C. NORMAN

Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England

(*Received* 2 *November* 1994; *accepted* 10 *January* 1995)

Abstract

Crystallization of the product of the reaction between impure samples of $In(NCS)_3$, prepared from $InCl_3$ and KSCN, and 2,2′-bipyridyl (bipy) in tetrahydrofuran solution gave the complex pentakis(tetrahydrofuran)-potassium (2,2′-bipyridyl)tetrakis(isothiocyanato)indate(III), $[K(C_4H_8O)_5][In(NCS)_4(C_{10}H_8N_2)]$, composed of a potassium cation coordinated by five thf ligands and one S atom of a thiocyanate group, and an octahedral indium-centred anion in which the bipy N atoms are *cis* and the four thiocyanates are bonded to indium through their N atoms. Crystallization of samples of impure $In(NCS)_3$ from pyridine in the presence of 18-crown-6 gave the compound (1,4,7,10,13,16-hexaoxacyclooctadecane)potassium bis(pyridine)tetrakis(isothiocyanato)-indate(III) pyridine solvate, $[K(C_{12}H_{24}O_6)][In(NCS)_4(C_5H_5N)_2].2C_5H_5N$, containing an octahedral indium-centred anion in which the pyridine ligands are *trans*. The potassium in both complexes arises from the contamination of $In(NCS)_3$ by the KSCN used in its preparation.

Comment

Structurally characterized thiocyanate complexes of indium(III) are not particularly common, the only reported examples being $[AsPh_4][In(NCS)_6]$ (1) (Einstein, Gilbert, Tuck & Vogel, 1976), $[K(18\text{-crown-}6)][K(18\text{-crown-}6)(H_2O)]_2[In(NCS)_6].2H_2O$ (2) (Zhan, Fan, Wang & Zhang, 1989), $[In(NCS)(OPPh_3)\{Mo(CO)_3(C_5H_5)\}_2]$ (3), $[In(NCS)(4\text{-picoline})\{Fe(CO)_2(C_5H_5)\}_2]$ (4) and $[K(18\text{-crown-}6)][In(NCS)_2\{Mo(CO)_3(C_5H_5)\}_2]$ (5) (Carmalt, Norman, Pember & Farrugia, 1995). In all cases, the thiocyanate group is

Acta Crystallographica Section C
ISSN 0108-2701 ©1995