

1257 reflections
71 parameters
H-atom parameters not refined

Atomic scattering factors
from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
Steffen, W. L. & Palenik, G. L. (1976). *Acta Cryst.* **B32**, 298–300.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Zn(1)	0.01069 (7)	0.25000	0.34742 (7)	0.020
I(1)	0.02501 (4)	0.02219 (5)	0.24298 (4)	0.034
N(1)	0.1443 (5)	0.2500	0.4588 (6)	0.021
N(1')	-0.1383 (6)	0.2500	0.4396 (5)	0.021
C(2)	0.1350 (7)	0.2500	0.5643 (7)	0.024
C(3)	0.2534 (9)	0.2500	0.6245 (8)	0.035
C(4)	0.3422 (8)	0.2500	0.5296 (8)	0.035
C(5)	0.2676 (7)	0.2500	0.4203 (7)	0.035
C(2')	-0.1972 (6)	0.1333 (8)	0.4744 (6)	0.043
C(3')	-0.3024 (7)	0.1713 (9)	0.5409 (7)	0.053

Table 2. *Geometric parameters* (\AA , $^\circ$)

Zn(1)—I(1)	2.557 (1)	N(1)—C(2)	1.280 (11)
Zn(1)—N(1')	2.025 (7)	N(1')—C(2')	1.384 (9)
N(1)—C(5)	1.474 (10)	C(3)—C(4)	1.528 (14)
C(2)—C(3)	1.528 (13)	C(2')—C(3')	1.486 (11)
C(4)—C(5)	1.569 (13)	C(3')—C(3'')	1.533 (13)
Zn(1)—N(1)	2.029 (7)		
I(1)—Zn(1)—N(1)	106.3 (1)	Zn(1)—N(1)—C(2)	126.8 (6)
N(1)—Zn(1)—N(1')	105.0 (3)	C(2)—N(1)—C(5)	113.2 (7)
Zn(1)—N(1)—C(5)	120.0 (6)	N(1)—C(2)—C(3)	113.7 (8)
Zn(1)—N(1')—C(2')	124.8 (4)	C(3)—C(4)—C(5)	106.0 (7)
C(2)—C(3)—C(4)	102.9 (8)	N(1')—C(2')—C(3')	110.4 (7)
N(1)—C(5)—C(4)	104.3 (7)	C(2')—N(1')—C(2'')	110.4 (7)
I(1)—Zn(1)—N(1')	108.9 (1)		

* Symmetry-generated atoms.

The crystal was cooled to 120 K using an Oxford Cryosystems device. Structure solution was obtained by direct methods using the program *MITHRIL* (Gilmore, 1984). Reliable H-atom positions could not be found from difference Fourier syntheses. Since the H-atom contributions were minimal, calculated positions were also excluded from the least-squares refinement. Calculations were performed using the Glasgow *GX* package (Mallinson & Muir, 1985).

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71364 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1044]

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Acta Cryst. (1993). **C49**, 2117–2119

Structure of



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Abstract

The structure of bis(*tert*-butylammonium) tetrachlorozincate-*tert*-butylammonium chloride (1/1) consists of $(\text{CH}_3)_3\text{CNH}_3^+$, ZnCl_4^{2-} and Cl^- ions. The distorted tetrahedral ZnCl_4^{2-} ion is surrounded by six cations with $\text{Cl}\cdots\text{N}$ distances of 3.19 (1)–3.38 (1) \AA , while the isolated Cl^- ion is surrounded by four cations with $\text{Cl}\cdots\text{N}$ distances of 3.21 (1)–3.33 (1) \AA . These short distances imply that the packing is stabilized by hydrogen bonds formed between the N and Cl atoms.

Comment

The title compound was investigated as part of a study on hydrogen bonding in alkylammonium tetrachlorozincates(II). Crystals of the title compound were obtained from an aqueous solution of $(\text{CH}_3)_3\text{CNH}_3\text{Cl}$ and ZnCl_2 in the molar ratios 3:1 or 2:1. To our knowledge, this is the first structural report of a double salt formed from an alkylamine- $\text{ZnCl}_2\text{-H}_2\text{O}$ system; the crystal structure of $(\text{NH}_4)_2\text{ZnCl}_4 \cdot \text{NH}_4\text{Cl}$ from the $\text{NH}_3\text{-ZnCl}_2\text{-H}_2\text{O}$ system has been reported (Klug & Alexander, 1944; Ohba, Shiokawa & Saito, 1987).

Cl(1), Cl(2) and Cl(4) in the ZnCl_4^{2-} ion are each considered to exhibit two hydrogen-bond contacts to the N atoms of the cations with the $\text{Cl}\cdots\text{N}$ distance of 3.19 (1)–3.38 (1) \AA , while Cl(3) does not seem to show any $\text{Cl}\cdots\text{H}\cdots\text{N}$ hydrogen-bond contacts; the shortest Cl(3) $\cdots\text{N}$ distance is 3.88 (1) \AA . Cl(3) has the shortest Zn—Cl bond in the ZnCl_4^{2-} ion; the anion is a distorted tetrahedron.

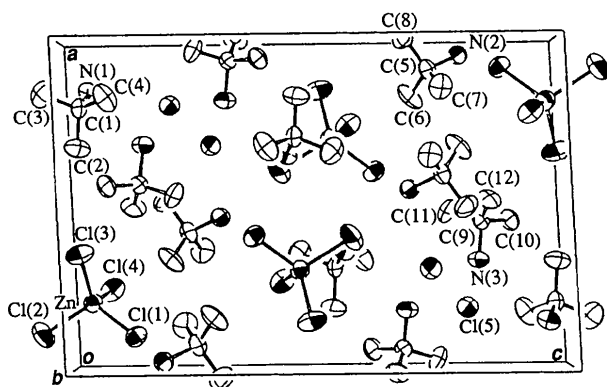


Fig. 1. An ORTEP (Johnson, 1976) perspective view along the *b* axis with the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Experimental

Crystal data

$3(\text{C}_4\text{H}_{12}\text{N})[\text{ZnCl}_4]\text{Cl}$

$M_r = 465.08$

Monoclinic

$P2_1/n$

$a = 12.362(3) \text{ \AA}$

$b = 10.440(3) \text{ \AA}$

$c = 18.641(5) \text{ \AA}$

$\beta = 92.29(2)^\circ$

$V = 2404(2) \text{ \AA}^3$

$Z = 4$

$D_x = 1.285 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 21\text{--}23^\circ$

$\mu = 1.606 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Prismatic

$0.35 \times 0.3 \times 0.3 \text{ mm}$

Colourless

Data collection

Rigaku AFC-5R diffractometer

$\omega/2\theta$ scans

Absorption correction:

empirical, ψ -scan correction

$T_{\min} = 0.74$, $T_{\max} = 1.00$

6086 measured reflections

5823 independent reflections

1914 observed reflections

$[I > 3.5\sigma(I)]$

$R_{\text{int}} = 0.065$

$\theta_{\text{max}} = 27.5^\circ$

$h = 0 \rightarrow 16$

$k = 0 \rightarrow 13$

$l = -24 \rightarrow 23$

3 standard reflections monitored every 97 reflections

intensity variation: +1.94%

Refinement

Refinement on F

$R = 0.070$

$wR = 0.076$

$S = 1.95$

1914 reflections

191 parameters

H-atom parameters not refined

$w = 4F_o^2/\sigma^2(F_o^2)$

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

$\Delta\rho_{\text{max}} = 0.64 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$

Extinction correction: secondary

Extinction coefficient: 1.87×10^{-6}

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

tion: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN* and *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*. Measurements were carried out at the X-ray Laboratory of Okayama University. No H atoms were included in the refinement.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Zn	0.1995 (1)	0.1777 (2)	0.0372 (1)	4.2 (1)
Cl(1)	0.0967 (3)	0.2622 (4)	0.1228 (2)	5.0 (2)
Cl(2)	0.1022 (4)	0.1691 (6)	-0.0689 (2)	8.9 (3)
Cl(3)	0.3502 (3)	0.2860 (4)	0.0186 (3)	6.7 (3)
Cl(4)	0.2355 (3)	-0.0275 (4)	0.0734 (2)	5.9 (3)
Cl(5)	0.1897 (3)	0.8672 (4)	0.7869 (2)	4.7 (2)
N(1)	0.8530 (9)	0.228 (1)	0.0528 (6)	4.2 (7)
N(2)	0.9598 (9)	0.026 (1)	0.8096 (6)	4.1 (7)
N(3)	0.3206 (9)	0.135 (1)	0.8290 (6)	4.4 (7)
C(1)	0.801 (1)	0.355 (2)	0.0339 (8)	5 (1)
C(2)	0.678 (1)	0.332 (2)	0.0264 (8)	6 (1)
C(3)	0.845 (1)	0.395 (2)	-0.038 (1)	7 (1)
C(4)	0.830 (1)	0.453 (1)	0.090 (1)	6 (1)
C(5)	0.915 (1)	0.098 (2)	0.7438 (8)	4 (1)
C(6)	0.833 (1)	0.007 (2)	0.707 (1)	7 (1)
C(7)	0.858 (1)	0.221 (1)	0.7678 (8)	6 (1)
C(8)	1.014 (1)	0.131 (2)	0.7002 (9)	7 (1)
C(9)	0.439 (1)	0.092 (1)	0.8398 (8)	3.6 (8)
C(10)	0.442 (1)	-0.008 (2)	0.9007 (8)	5 (1)
C(11)	0.472 (1)	0.028 (1)	0.7715 (8)	5 (1)
C(12)	0.507 (1)	0.210 (1)	0.8557 (8)	5 (1)

Table 2. Geometric parameters (\AA , $^\circ$)

Zn—Cl(1)	2.259 (4)	Cl(1)—C(3)	1.52 (2)
Zn—Cl(2)	2.275 (5)	Cl(1)—C(4)	1.50 (2)
Zn—Cl(3)	2.218 (4)	C(5)—C(6)	1.52 (2)
Zn—Cl(4)	2.284 (5)	C(5)—C(7)	1.54 (2)
N(1)—C(1)	1.51 (2)	C(5)—C(8)	1.54 (2)
N(2)—C(5)	1.53 (2)	C(9)—C(10)	1.54 (2)
N(3)—C(9)	1.54 (2)	C(9)—C(11)	1.51 (2)
Cl(1)—C(2)	1.54 (2)	C(9)—C(12)	1.52 (2)
Cl(1)···N(1)	3.25 (1)	Cl(4)···N(2 ⁱ)	3.32 (1)
Cl(1)···N(2 ⁱ)	3.34 (1)	Cl(5)···N(1 ⁱ)	3.21 (1)
Cl(2)···N(2)	3.19 (1)	Cl(5)···N(2)	3.33 (1)
Cl(2)···N(3)	3.38 (1)	Cl(5)···N(3 ⁱⁱ)	3.25 (1)
Cl(3)···N(3)	3.88 (1)	Cl(5)···N(3)	3.31 (1)
Cl(4)···N(1 ⁱ)	3.30 (1)		
Cl(1)—Zn—Cl(2)	109.7 (2)	N(2)—C(5)—C(6)	106 (1)
Cl(1)—Zn—Cl(3)	114.3 (2)	N(2)—C(5)—C(7)	110 (1)
Cl(1)—Zn—Cl(4)	105.4 (2)	N(2)—C(5)—C(8)	105 (1)
Cl(2)—Zn—Cl(3)	107.6 (2)	C(6)—C(5)—C(7)	110 (1)
Cl(2)—Zn—Cl(4)	108.0 (2)	C(6)—C(5)—C(8)	116 (1)
Cl(3)—Zn—Cl(4)	111.7 (2)	C(7)—C(5)—C(8)	110 (1)
N(1)—C(1)—C(2)	107 (1)	N(3)—C(9)—C(10)	107 (1)
N(1)—C(1)—C(3)	107 (1)	N(3)—C(9)—C(11)	108 (1)
N(1)—C(1)—C(4)	110 (1)	N(3)—C(9)—C(12)	108 (1)
C(2)—C(1)—C(3)	110 (1)	C(10)—C(9)—C(11)	109 (1)
C(2)—C(1)—C(4)	113 (1)	C(10)—C(9)—C(12)	114 (1)
C(3)—C(1)—C(4)	110 (1)	C(11)—C(9)—C(12)	111 (1)

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

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71408 (21 pp.). Copies may be obtained through The Technical Editor, *International Union of Crystallography*, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1035]

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduc-

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Acta Cryst. (1993). **C49**, 2119–2121

Structure of Bis(triethylammonium) Phenylphosphonosulfate

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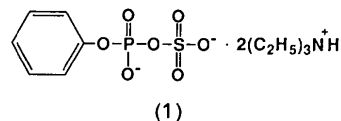
Abstract

Each N—H bond of the two triethylammonium cations faces each of the non-bridging O atoms of the monoanionic phosphate moiety in the phenylphosphonosulfate dianion. The N...O distances of 2.676 (9) and 2.736 (9) Å show the existence of intermolecular N—H...O hydrogen bonds. No direct interactions exist between the two cations and the monoanionic sulfate group.

Comment

Many structural studies have been reported for compounds of biologically important mono-, di- or triphosphate esters (*e.g.* Calvo, 1967; Aoki, 1979; Kennard *et al.*, 1971). The phosphatosulfate ester bond is very important in biological sulfate-transfer reactions (Peck, 1974), but its structural study has

not been reported. In this paper we report the structure of the title compound (1) and discuss the nature of the phosphatosulfate chain.



The phenyl phosphatosulfate (PPS) was synthesized as described in the literature (Benkovic & Hevey, 1970; Tagaki, Eiki & Tanaka, 1971) and then converted to the title salt. Colourless crystals for data collection were prepared by the dissolution of the salt in acetone followed by the addition of ethyl acetate. Elemental analysis found: C, 47.53; H, 8.21; N, 6.18; S, 6.95%. Calculated for $C_{18}H_{37}N_2O_7PS$: C, 47.36; H, 8.17; N, 6.14; S, 7.02%.

The two triethylammonium cations neutralize the two negative charges of the dianion of (1). As seen from Fig. 1, each of the atoms N(1) and N(2) has a tetrahedral configuration (including the N—H⁺ bond). Each of the N(2)—H(37) and N(1)—H(36) bonds faces the two non-bridging O atoms of the monoanionic phosphate moiety, O(3) and O(2), respectively; the intermolecular bond angles N(2)—H(37)...O(3) and N(1)—H(36)...O(2) are 172.9 (10) and 153.0 (9)°, respectively. The intermolecular distances O(2)...H(36) and O(3)...H(37) are 1.720 (11) and 1.592 (11) Å, N(2)...O(3) and N(1)...O(2) are 2.676 (9) and 2.736 (9) Å, respectively. These values correspond to the hydrogen-bond lengths between each triethylammonium cation and the nearest non-bridging O atom of PPS^{2-} . The literature values are as follows: (i) the N—H...O hydrogen-bond lengths

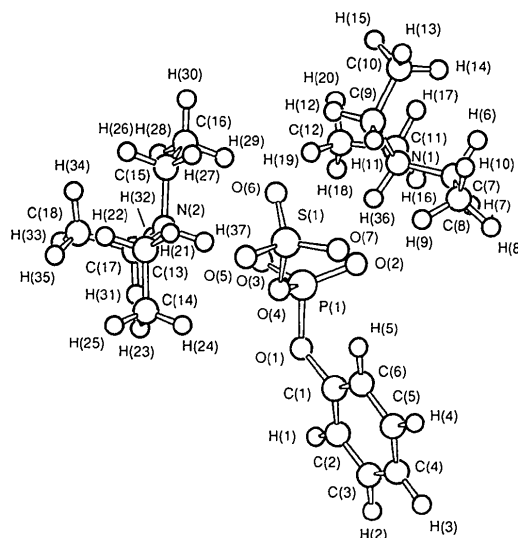


Fig. 1. Molecular structure of the title compound with atomic numbering scheme.