$S = 1.580$
2058 reflections
155 parameters
H-atom parameters riding
$w = 4F_o^2/\sigma^2(F_o^2)$

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)*

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

	x	y	z	$U_{\rm eq}$
Sr(1)	0	0.13280 (3)	1/4	0.0503 (1)
O(1)	0	−0.0641 (3)	1/4	0.082 (1)
C(1)	0.1510 (2)	0.1492 (2)	0.1708 (2)	0.0562 (9)
C(2)	0.1161 (2)	0.2499 (2)	0.1726 (2)	0.0540 (9)
C(3)	0.1484 (2)	0.2827 (2)	0.2475 (2)	0.0540 (9)
C(4)	0.2033 (2)	0.2035 (3)	0.2922 (2)	0.0554 (9)
C(5)	0.2048 (2)	0.1205 (2)	0.2452 (2)	0.0583 (9)
C(6)	0.1431 (3)	0.0859 (3)	0.1023 (2)	0.079 (1)
C(7)	0.0923 (4)	−0.0156 (4)	0.1007 (3)	0.119 (2)
C(8)	0.2477 (4)	0.0713 (5)	0.0906 (3)	0.149 (3)
C(9)	0.0644 (3)	0.3162 (3)	0.1063 (2)	0.068 (1)
C(10)	0.0007 (3)	0.4018 (3)	0.1223 (3)	0.100 (2)
C(11)	0.1419 (4)	0.3599 (4)	0.0705 (3)	0.106 (2)
C(12)	0.2480 (3)	0.2085 (3)	0.3755 (2)	0.071 (1)
C(13)	0.1889 (3)	0.1418 (3)	0.4150 (2)	0.086 (1)
C(14)	0.3614 (3)	0.1849 (4)	0.4021 (2)	0.109 (2)
C(15)	0.0862 (3)	−0.1277 (3)	0.2870 (3)	0.107 (2)
C(16)	0.0503 (4)	−0.2323 (4)	0.2806 (3)	0.130 (2)

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

Sr(1)—O(1)	2.571 (3)	C(1)—C(2)	1.402 (4)
Sr(1)—C(1)	2.887 (3)	C(1)—C(5)	1.427 (4)
Sr(1)—C(2)	2.889 (3)	C(2)—C(3)	1.417 (4)
Sr(1)—C(3)	2.818 (3)	C(3)—C(4)	1.399 (4)
Sr(1)—C(4)	2.785 (3)	C(4)—C(5)	1.406 (4)
Sr(1)—C(5)	2.809 (3)		
Sr(1)—O(1)—C(15)	125.5 (2)	C(2)—C(3)—C(4)	109.1 (3)
C(15)—O(1)—C(15$^{\rm i}$)	109.0 (4)	C(3)—C(4)—C(5)	107.2 (3)
C(2)—C(1)—C(5)	107.3 (3)	C(1)—C(5)—C(4)	108.7 (3)
C(1)—C(2)—C(3)	107.7 (3)		

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985), *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dicaesium Ethyltrimethylammonium Heptaphosphide–Ammonia (1/2)

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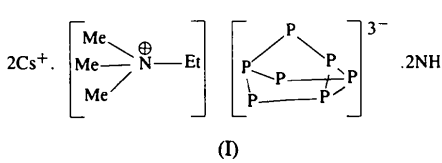
Abstract

The exchange of one Cs^+ cation of Cs_3P_7 for $NEtMe_3^+$ in liquid ammonia gives the title compound, $(NEtMe_3)Cs_2P_7.2NH_3$. The crystal structure determination shows the existence of corrugated two-dimensionally infinite $Cs_2P_7^-$ layers.

Comment

The title compound, (I), was prepared and its structure determined in the course of investigations of the reactions of alkali metal phosphides, $M_3^1P_{11}$ and $M_3^1P_7$ (M^1 = Na, K, Rb, Cs), with quaternary alkyl ammonium salts.

One Cs^+ cation of Cs_3P_7 was exchanged for $NEtMe_3^+$ in liquid ammonia yielding $(NEtMe_3)Cs_2P_7.2NH_3$. The



(I)

crystal structure determination shows the existence of corrugated two-dimensionally infinite $Cs_2P_7^-$ layers (Figs. 1 and 2), which are similar to analogous layers with different quaternary ammonium cations observed previously (Korber & Daniels, 1996). One ammonia molecule of solvation completes the coordination sphere of each of the two crystallographically inequivalent Cs^+ cations, which have close contacts to eight P atoms of three different P_7^{3-} cages (Fig. 3). The corresponding Cs1···P distances range from 3.516 (2) to 3.935 (2) Å. The next closest distance after these initial eight is nearly 18% larger [Cs1···P4 4.642 (2) Å]. The Cs2···P distances range from 3.545 (2) to 3.893 (2) Å [next closest contact 4.585 (2) Å]. Both Cs^+ cations cap the trapezoidal sides of the heptaphosphanortricyclane cage in a η^4-like coordination. The Cs···P distances show a marked preference for the twofold-linked P atoms as coordinating atoms. These are formally negatively charged and seem to have superior donor properties towards the Cs^+ cations.

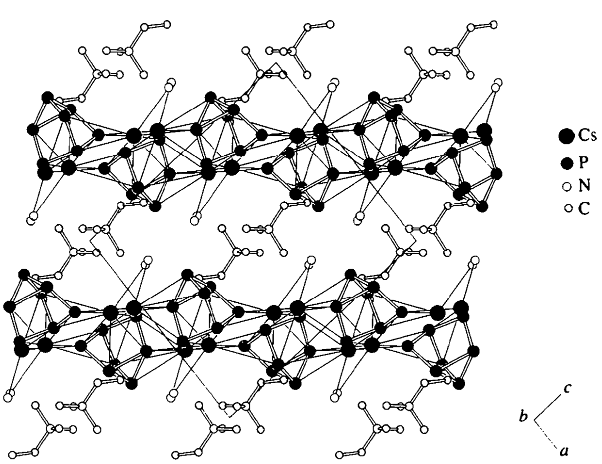


Fig. 1. View of (I) showing the stacking of the $Cs_2P_7^-$ layers perpendicular to the *b* axis.

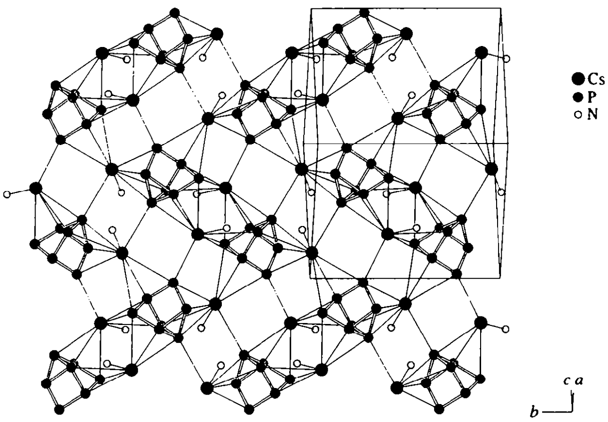


Fig. 2. View perpendicular to the $Cs_2P_7^-$ layers. The ethyltrimethylammonium cations are not shown.

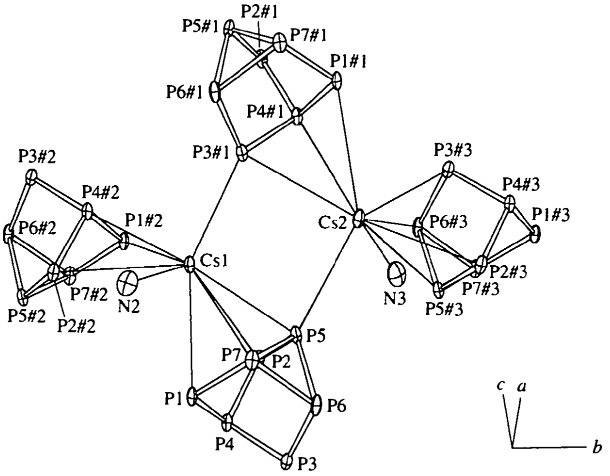


Fig. 3. *ORTEP*II (Johnson, 1971) plot (50% probability level) of the two crystallographically inequivalent Cs^+ cations and the coordinating cage anions. [Symmetry operations: (#1) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (#2) $-x, -y, -z + 1$; (#3) $-x, -y + 1, -z + 1$.]

The endocyclic bond lengths and angles reveal small but significant deviations from the ideal $3m$–C_{3v} symmetry of the unperturbed cage (von Schnering & Hönle, 1988). This distortion can be related to Cs···P interactions. The single bond in the triangular P_3 base of the cage, which is not bridged by a Cs cation, is significantly shorter [P6—P7 2.262 (3) Å] than its counterparts [P5—P7 2.283 (2) and P6—P5 2.293 (3) Å]. This results in a smaller P1—P4—P3 angle [101.47 (9)°] compared with the P3—P4—P2 [102.4 (1)°] and P2—P4—P1 [102.8 (1)°] angles. The height, *h*, of the cage (distance between the centre of the basal triangle and the apical P atom) is 2.987 (2) Å. It has been used as a measure of the ionic character for the nortricyclane cage (von Schnering & Hönle, 1988). It is about 1.8 pm larger compared with Cs_3P_7 (h = 2.969 Å; von Schnering, Meyer & Hönle, 1987) which at first seems to contradict the argument that an increase of charge transfer to the twofold-linked P atoms should result in a larger repulsion between these atoms and consequently in a lower value of *h*. It is probable, however, that a value of approximately 2.97 Å represents a lower limit generated by the covalent forces maintaining the bond lengths and bond angles of the cage. The slightly larger height of the cage in $(NEtMe_3)Cs_2P_7.2NH_3$ may be the result of the low temperature maintained during the data collection, which usually leads to larger values for atomic distances due to smaller displacement parameters.

Experimental

Cs_3P_7 (312.3 mg, 0.000507 mol) was allowed to react with ethyltrimethylammonium iodide (338.4 mg, 0.00157 mol) in liquid ammonia (about 30 ml) in a U-shaped vessel, with a glass frit (porosity 3) separating the two components. Pale yellow crystalline blocks were obtained after six weeks. The crystals turned immediately opaque upon removal of the solvent. The product is unstable at room temperature and highly reactive towards air and moisture. During the selection and mounting of the crystal, loss of solvent and decomposition was prevented by using the low-temperature method developed by Kottke & Stalke (1993). Cs_3P_7 was synthesized from the elements in a sealed glass ampoule following the procedure established previously by von Schnering, Meyer & Hönle (1987). Red phosphorus was obtained from Hoechst (electronic grade), caesium was synthesized by reduction of the chlorides with calcium (Hackspill, 1928) and purified by double distillation.

Crystal data

$2Cs^+.C_5H_{14}N^+.P_7^{3-}.2NH_3$
$M_r = 604.86$
Monoclinic
$P2_1/n$
$a = 11.890(2)$ Å
$b = 12.286(3)$ Å
$c = 13.579(3)$ Å
$\beta = 94.32(2)°$
$V = 1978.0(7)$ Å^3
$Z = 4$
$D_x = 2.031$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7–14°$
$\mu = 4.238$ mm^{-1}
$T = 123(2)$ K
Block
Crystal size not measured
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
Variable-speed $\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
$T_{\min} = 0.8247$, $T_{\max} = 0.9995$
9174 measured reflections
2743 independent reflections

2568 observed reflections $[I > 2\sigma(I)]$
$R_{\text{int}} = 0.075$
$\theta_{\max} = 23.01°$
$h = -13 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0408$
$wR(F^2) = 0.1073$
$S = 1.199$
2743 reflections
177 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 3.3792P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.008$
$\Delta\rho_{\max} = 1.811$ e Å^{-3}
$\Delta\rho_{\min} = -1.404$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0007 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
Cs1	0.14530 (3)	0.07774 (3)	0.52751 (3)	0.0168 (2)
Cs2	0.20148 (4)	0.47459 (3)	0.61113 (3)	0.0195 (2)
P1	−0.0221 (2)	0.07751 (13)	0.27669 (13)	0.0165 (4)
P2	−0.1117 (2)	0.24042 (14)	0.45857 (12)	0.0170 (4)
P3	−0.18634 (15)	0.29576 (14)	0.21842 (12)	0.0168 (4)
P4	−0.17270 (15)	0.16113 (14)	0.32189 (12)	0.0156 (4)
P5	0.03070 (15)	0.32197 (14)	0.40585 (12)	0.0175 (4)
P6	−0.0197 (2)	0.35925 (14)	0.24304 (12)	0.0181 (4)
P7	0.08956 (15)	0.21295 (14)	0.28366 (13)	0.0178 (4)
N1	−0.0119 (5)	0.2493 (5)	0.9236 (4)	0.0178 (13)
C1	0.0171 (6)	0.2261 (6)	0.8191 (5)	0.025 (2)
C2	0.0595 (7)	0.1785 (7)	0.9917 (6)	0.040 (2)
C3	0.0135 (7)	0.3664 (6)	0.9504 (5)	0.032 (2)
C4	−0.1339 (6)	0.2255 (7)	0.9354 (6)	0.031 (2)
C5	−0.0431 (7)	0.2968 (7)	0.7429 (5)	0.039 (2)
N2	0.2572 (6)	−0.0647 (6)	0.3686 (5)	0.033 (2)
N3	0.2498 (6)	0.5385 (6)	0.3884 (5)	0.033 (2)

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

Cs1—N2	3.150 (7)	Cs2—P3^{i}	3.826 (2)
Cs1—P3^{i}	3.516 (2)	Cs2—P1^{i}	3.893 (2)
Cs1—P4^{ii}	3.578 (2)	P1—P7	2.126 (3)
Cs1—P5	3.640 (2)	P1—P4	2.192 (3)
Cs1—P1^{ii}	3.666 (2)	P2—P5	2.136 (2)
Cs1—P2	3.712 (2)	P2—P4	2.172 (2)
Cs1—P7	3.719 (2)	P3—P6	2.132 (3)
Cs1—P1	3.813 (2)	P3—P4	2.168 (2)
Cs1—P2^{ii}	3.935 (2)	P5—P7	2.283 (2)
Cs2—N3	3.218 (6)	P5—P6	2.293 (3)
Cs2—P4^{i}	3.545 (2)	P6—P7	2.262 (3)
Cs2—P6^{iii}	3.661 (2)	N1—C2	1.49 (1)
Cs2—P3^{iii}	3.662 (2)	N1—C4	1.500 (9)
Cs2—P5^{iii}	3.718 (2)	N1—C3	1.510 (9)
Cs2—P2^{iii}	3.761 (2)	N1—C1	1.512 (8)
Cs2—P5	3.815 (2)	C1—C5	1.49 (1)
P7—P1—P4	98.12 (9)	P7—P6—P5	60.16 (8)
P5—P2—P4	98.40 (9)	P1—P7—P6	105.4 (1)
P6—P3—P4	98.9 (1)	P1—P7—P5	105.48 (9)
P3—P4—P2	102.4 (1)	P6—P7—P5	60.60 (8)
P3—P4—P1	101.47 (9)	C2—N1—C4	109.3 (6)
P2—P4—P1	102.8 (1)	C2—N1—C3	108.2 (6)
P2—P5—P7	105.21 (9)	C4—N1—C3	109.7 (6)
P2—P5—P6	105.1 (1)	C2—N1—C1	108.3 (6)
P7—P5—P6	59.25 (8)	C4—N1—C1	110.8 (6)
P3—P6—P7	104.9 (1)	C3—N1—C1	110.5 (5)
P3—P6—P5	104.51 (9)	C5—C1—N1	114.2 (6)

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

For the ammonium cation, H atoms were positioned riding on their attached C atoms, with a common isotropic displacement parameter for all CH_2 and CH_3 groups, while for NH_3, H atoms were restrained to have the same intramolecular N—H and H···H distances in both inequivalent molecules. The chemical nature of the compound (immediate loss of solvent below 243 K) made measurement of the crystal density impossible by standard methods. Only a very rough estimate of the crystal size was possible due to the mounting of the extremely sensitive crystal in opaque perfluorether oil. We do not wish to give the appearance of precision by supplying numbers of which we are very unsure. Maximum and minimum residual electron densities were located next to the heavy atoms (Cs) at distances of less than 100 pm.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CELDIM* in *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1122). 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**, 2457–2460

Aqua(2,2′-bipyridyl-*N*,*N*′)(thiodiacetato-*O*,*O*′,*S*)zinc(II) Tetrahydrate

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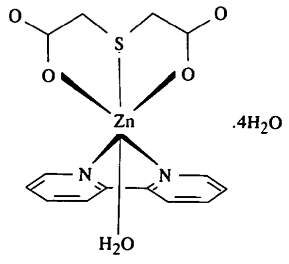
Abstract

The title complex, aqua(2,2′-bipyridyl-*N*,*N*′)(3-thiapentanedioate-*O*,*S*,*O*′)zinc(II) tetrahydrate, $[Zn(C_4H_4O_4S)(C_{10}H_8N_2)(H_2O)].4H_2O$, is mononuclear with a coordination sphere consisting of one S, two N and three O atoms. The Zn atom is linked to a tridentate thiodiacetate ligand, a bidentate 2,2′-bipyridine ligand and an aqua ligand resulting in a slightly distorted octahedral coordination geometry. The molecular units are linked together in the crystal by an extensive hydrogen-bonding network and by intermolecular S···S interactions.

Comment

Current interest in zinc compounds with thioether sulfur ligands is due in part to their relevance as structural models in biological systems (Bouwman, Evans, de Graaff, Kooijman, Poinsot, Rabu, Reedijk & Spek, 1995; Haanstra, Driessen, Reedijk, Turpeinen & Hämäläinen, 1989). Very few crystal structures of zinc complexes with acyclic ligands having thioether groups as coordinating agents have been reported so far (Drew, Rice & Timewell, 1975; Teixidor, Escriche, Casabo, Molins & Miravitlles, 1986; Mangia, Nardelli, Palmieri & Pellizzi, 1972). Among these, triaquazinc(II) thiodiacetate monohydrate, $[Zn\{S(CH_2COO)_2\}(H_2O)_3].H_2O$, was found to be monomeric, with a distorted octahedral ZnO_5S core and a Zn—S bond length of 2.601 (2) Å (Drew *et al.*, 1975). The results of the present study include the preparation, characterization and X-ray structure determination of the title complex, $[Zn\{S(CH_2COO)_2\}(2,2'\text{-bpy})(H_2O)].4H_2O$ (bpy is bipyridine), hereafter (1). It was of interest to further examine the coordination behaviour of the thiodiacetate ligand towards the 'hard' Zn^{II} metal ion and to study its dependence on the ligands associated with the metal centre.



(1)

The structure of (1) and the atomic numbering scheme are shown in Fig. 1. The Zn atom has octahedral geometry to a reasonably good approximation, comprised of the two carboxylate O atoms of the thiodiacetate [Zn—O1 2.047 (2), Zn—O5 2.067 (2) Å and O1—Zn—O5 95.94 (6)°], the thioether S atom of the thiodiacetate [Zn—S3 2.618 (1) Å], two N atoms of the 2,2′-bpy ligand [Zn—N1 2.124 (2), Zn—N2 2.167 (2) Å and

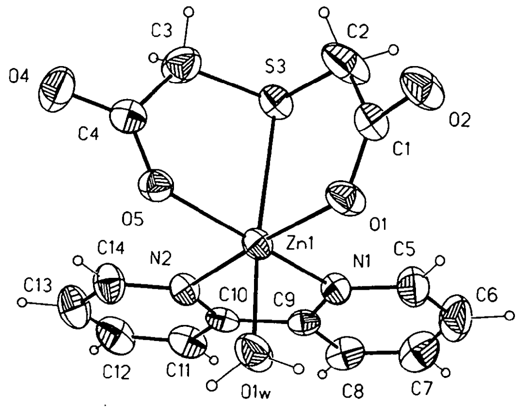


Fig. 1. Molecular diagram showing the labelling scheme used. Displacement ellipsoids are drawn at the 50% probability level.