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X-ray Crystallography of the $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$ Compounds. I. Crystal Structure of the Geminal 2,2,4-Trichloro-4,6,6-trisdimethylaminocyclotriphosphazatriene

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The crystal structure of the geminal 2,2,4-trichloro-4,6,6-trisdimethylaminocyclotriphosphazatriene, $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$, has been determined by the symbolic addition procedure, and has been refined by least-squares to $R = 0.05$ for the 2495 observed reflexions. The unit cell is monoclinic, $P2_1/n$, with $a = 15.867$, $b = 11.869$, $c = 8.861$ Å, $\beta = 93^\circ 44'$, $Z = 4$. The P_3N_3 ring has a distorted boat conformation. The two bonds of each P-N-P segment are of different lengths, 1.546 ± 0.001 and 1.607 ± 0.001 Å for two of the segments, and 1.563 and 1.592 Å for the third, but the average of the two bonds in each segment is 1.577 Å. The endocyclic N-P(NMe₂)₂-N angle is only 113.1° , while the N-PCl₂-N and N-PCl(NMe₂)-N angles are 120.7 and 119.0° . The P-N ligands are of nearly equal lengths 1.628, 1.639, and 1.642 ($\sigma = 0.004$) Å, but the P-Cl ligands are of significantly different lengths 1.992, 2.014 and 2.051 ($\sigma = 0.002$) Å.

Introduction

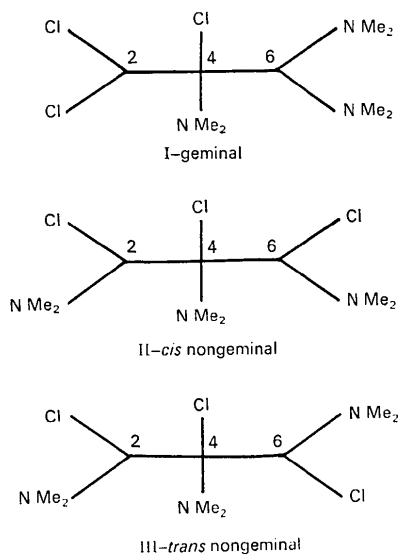
The X-ray crystal structure analysis of small phosphonitrilic systems is intended to enhance the understanding of the P-N bonding mechanism, since the theoretical concepts of valency in these compounds are usually complicated due to the wide variety of *d*-orbitals and the different symmetries of the *p*- and *d*-orbitals, Paddock (1964). Beside the academic interest in the valency problem, there has been an increasing industrial interest in the phosphonitriles because of their use as fire proofing reagents (Shaw, 1968).

In all the trimeric phosphonitriles examined so far by X-rays, the molecular formulae were of the types

$\text{R}_6\text{P}_3\text{N}_3$ and $\text{R}_4\text{R}'_2\text{P}_3\text{N}_3$, with two like substituents (R_2 or R'_2) at each P atom. A study of the crystal structure of $\text{Cl}_5\text{FP}_3\text{N}_3$ by Olthof (1969) did not quite achieve the objectives of the analysis since the F atom was found to be equally distributed over the six halogen positions. The present series on the $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$ compounds has been undertaken in order to examine the stereochemistry of the P_3N_3 ring as the positions of the substituents on the ring are altered. These compounds were characterized by Keat & Shaw (1965) who also supplied suitable crystals for the X-ray analysis. The three compounds of this series are: (I) geminal 2,2,4-trichloro-4,6,6-trisdimethylamino-, (II) *cis* non-geminal 2,4,6-trichloro-2,4,6-trisdimethylamino- and (III) *trans* non-geminal 2,4,6-trichloro-2,4,6-trisdimethylamino-cyclotriphosphazatriene. The crystal

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structure of the geminal compound (I) is presented in this paper, and that of the *cis* non-geminal compound (II) is now under study.



Experimental

Crystals of the geminal compound (I) which were used for the data collection were cut from larger crystals into approximate cubes of 0.2–0.3 mm length. The quality of the crystals deteriorated on exposure to X-rays, and four crystals in total had to be used. On exposure, the crystals became opaque, the profile of the diffracted intensities broadened, and the integrated intensities dropped steadily. Similar changes were also noted for crystals of the *cis* non-geminal compound (II).

The space group assignment was based on precession photographs. The unit-cell dimensions and the intensity data were measured on a Picker automatic diffractometer with Mo radiation and Nb filters, placed before the crystal, and with **b** along the φ axis of the instrument. The cell constants were derived from the 2θ and φ values of a few axial reflexions measured with a narrow slit at a take off angle of 1° . The integrated intensities were measured at a 2θ scan rate of $2^\circ/\text{min}$ over a scan range of 2.0 or 2.4° in 2θ , and the background was measured for 20 sec at the start and at the end of each scan. The 004 and 130 reflexions were monitored every 20–40 reflexions. The crystal density was obtained by flotation in a solution of carbon tetrachloride and toluene at 20°C . The crystal data are presented in Table 1.

In total, 3809 permissible non-equivalent reflexions within $2\theta = 55^\circ$ ($\sin \theta/\lambda = 0.65 \text{ \AA}^{-1}$) were scanned, but only 2495 reflexions (65.4%) were observed above threshold. The very strong reflexions were remeasured at the end with a lower current setting. The Lorentz-polarization corrections were applied, but the absorption corrections for Mo radiation were considered to be negligible.

Table 1. *Crystal data*

<i>a</i>	15.867 (5) Å	$\text{C}_6\text{H}_{18}\text{N}_6\text{P}_3\text{Cl}_3$	
<i>b</i>	11.869 (5)	M.W.	373.53 g/mole
<i>c</i>	8.861 (6)	Space group	$P2_1/n$
β	$93.73 (6)^\circ$	<i>Z</i>	4
<i>U</i>	1665.21 \AA^3	<i>F</i> (000)	768 electrons
<i>D_x</i>	1.490 g.cm^{-3}	$\mu(\text{Cu})$	76.3 cm^{-1}
<i>D_m</i>	1.493 g.cm^{-3}	$\mu(\text{Mo})$	8.3 cm^{-1}

Systematic absences: $h0l$ when $h+l=2n+1$;
 $0k0$ when $k=2n+1$.

Structure determination

The structure was determined by the direct method of symbolic addition, as described by Karle & Karle (1963) and Karle & Karle (1966). In attempting to phase the 170 reflexions with $|E| > 2.0$, the computer program selected 3, 11, 3, $\bar{1}2, 3, 1$, and 465 as the origin-defining reflexions, and assigned symbols *A*, *B*, *C* to three others at different stages when they were needed. The value of each symbol and symbol-product was determined independently from the multiple sign indications accumulated for each reflexion during the phasing process, as described by Ahmed (1970). This procedure gave self consistent signs, *i.e.* satisfying identities such as $s(A) \cdot s(B) = s(AB)$, and the phases of the 170 reflexions were determined unambiguously. Using these phases and the Σ_2 relationships, phases were derived for 323 of the 327 reflexions with $2.0 \geq |E| \geq 1.5$. The 493 accepted signs were later found to be all correct.

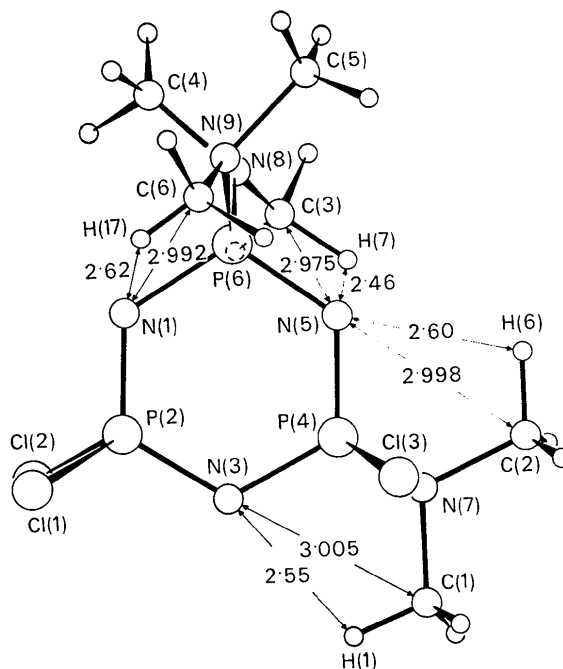


Fig. 1. A view of the molecule down the normal to the phosphazene ring, with the short intramolecular distances (Å) indicated.

The positions of the P, N, and Cl atoms were taken from the *E* map, and those of the C atoms were accepted from the first Fourier map. The *R* index for this trial structure was 0.22, and it was reduced to 0.08 after six anisotropic cycles of block-diagonal least-

squares. A difference map calculated at this stage showed all the H atoms with peak heights 0.3–0.5 e.Å⁻³. The refinement was continued until *R* for the observed reflexions was reduced to 0.050, and the shifts in the atomic parameters were < 0.3σ for P, N,

Table 2. Fractional coordinates, vibration tensor components (Å²) for the expression $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$, and their e.s.d.'s

	All quantities × 10 ⁴ .									
	X	Y	Z	U11	U22	U33	2U23	2U13	2U12	
N(1)	4036(2)	2441(3)	6804(4)	434(19)	783(27)	419(19)	-33(37)	-140(30)	-436(37)	
P(2)	3755(1)	2984(1)	5251(1)	377(5)	502(6)	406(6)	25(10)	15(8)	-257(10)	
N(3)	3015(2)	2550(3)	4248(4)	467(19)	664(24)	395(18)	245(34)	-171(30)	-359(35)	
P(4)	2515(1)	1481(1)	4808(1)	324(5)	475(6)	368(5)	10(10)	-64(8)	-157(10)	
N(5)	2708(2)	1048(3)	6441(4)	479(20)	704(25)	392(18)	26(35)	-138(30)	-429(36)	
P(6)	3478(1)	1488(1)	7553(1)	393(5)	509(6)	323(5)	54(10)	-70(8)	-43(10)	
Cl(1)	4810(1)	2968(1)	4000(1)	546(8)	1239(13)	644(7)	-67(17)	388(12)	-546(16)	
Cl(2)	3657(1)	4641(1)	5500(2)	1148(13)	480(7)	1007(11)	-48(16)	-212(19)	-133(16)	
Cl(3)	2775(1)	199(1)	3359(1)	887(10)	663(9)	631(7)	-318(14)	236(13)	165(14)	
N(7)	1507(2)	1710(3)	4492(4)	392(18)	588(24)	622(22)	114(37)	-85(32)	-74(33)	
N(8)	3076(2)	1922(3)	9110(4)	587(22)	632(24)	389(18)	-95(35)	84(31)	-20(38)	
N(9)	4144(2)	498(3)	8139(4)	529(22)	637(25)	538(22)	-20(39)	-150(35)	225(38)	
C(1)	1215(3)	2217(5)	3061(6)	474(27)	1009(44)	781(36)	265(66)	-367(49)	125(58)	
C(2)	928(3)	870(6)	5055(7)	444(28)	962(45)	1220(50)	311(77)	124(59)	-314(58)	
C(3)	2261(4)	2485(6)	9023(7)	760(37)	1031(49)	834(40)	-484(72)	180(61)	452(68)	
C(4)	3654(4)	2335(5)	10324(5)	889(38)	850(40)	402(24)	-337(53)	-169(48)	-33(64)	
C(5)	3824(4)	-401(5)	9072(7)	863(40)	643(34)	874(39)	427(62)	-255(62)	74(61)	
C(6)	4735(4)	104(6)	7072(6)	772(37)	1057(49)	686(34)	-270(68)	-78(57)	739(70)	
H(1)	1610(28)	2830(49)	2718(58)	481(314)	1552(555)	1117(433)	1020(830)	-1064(595)	-1087(706)	
H(2)	1303(32)	1674(50)	2229(57)	766(392)	1550(586)	957(426)	-779(817)	114(639)	124(800)	
H(3)	681(30)	2517(42)	3063(50)	818(374)	1009(443)	606(320)	448(630)	-447(557)	-692(651)	
H(4)	554(35)	321(56)	4380(65)	846(441)	1544(614)	1171(499)	-422(917)	331(744)	-114(844)	
H(5)	476(34)	1216(57)	5293(83)	520(379)	1598(671)	2637(830)	2303(1234)	403(918)	54(795)	
H(6)	1109(34)	548(53)	6134(61)	1024(468)	1691(627)	956(433)	1412(882)	-1088(719)	-1199(897)	
H(7)	1856(35)	2077(54)	8216(63)	980(455)	1229(532)	1204(496)	384(854)	-566(749)	-127(820)	
H(8)	1984(40)	2368(63)	10035(72)	1319(603)	1943(781)	1377(593)	96(1114)	692(951)	1079(1113)	
H(9)	2235(38)	3270(62)	8871(68)	987(486)	2106(788)	1153(509)	-520(1065)	432(811)	-131(1010)	
H(10)	3608(35)	2344(57)	11323(53)	1133(486)	1974(709)	520(349)	441(814)	160(658)	-558(958)	
H(11)	4212(32)	2070(49)	10346(55)	965(417)	1345(524)	722(361)	-546(740)	-1043(623)	318(785)	
H(12)	3751(32)	3187(46)	10165(54)	981(417)	1076(465)	713(355)	133(678)	-903(613)	-687(737)	
H(13)	3548(48)	-960(53)	8445(69)	2514(816)	1028(515)	1073(486)	-331(839)	-2363(1052)	142(1101)	
H(14)	3434(39)	-120(41)	9947(61)	1752(602)	384(335)	1192(476)	244(654)	1010(878)	156(733)	
H(15)	4240(31)	-692(42)	9556(51)	927(400)	820(396)	818(375)	1269(654)	-181(624)	391(654)	
H(16)	5225(35)	-202(53)	7625(55)	1018(445)	1649(617)	686(375)	63(799)	-667(658)	713(866)	
H(17)	5002(35)	661(52)	6636(57)	1069(463)	1623(594)	751(388)	-1645(806)	396(684)	236(867)	
H(18)	4408(36)	-389(54)	6273(62)	1222(507)	1584(612)	1008(454)	-1617(883)	-6(757)	1226(920)	

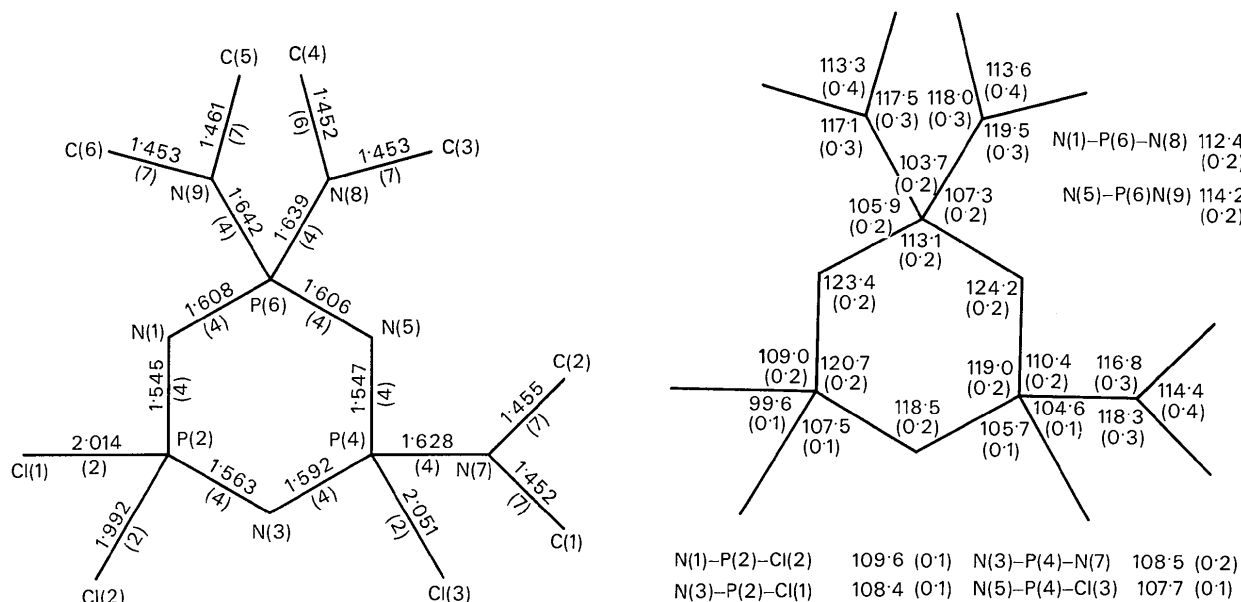


Fig. 2. Bond lengths (Å) and angles (°), and their e.s.d.'s in parentheses. E.s.d.'s of bond lengths are × 10³.

Table 3. Structure factor data (x 10)

* Indicates unobserved reflexions and |F_{obs}| in place of |F_o|.

Main body of the document containing a large grid of numerical data representing structure factor values for various hkl reflections. The grid is organized in columns by h, k, and l indices and contains numerical values for each reflection, with asterisks marking unobserved reflexions.

stituents and the ring. In this structure, the NC_2 group substituted at P(4) is rotated by only 1° around the P(4)–N(7) bond, while those at P(6) are rotated by angles of 50 and 53° round the P(6)–N(8) and P(6)–N(9) bonds respectively.

The equations of the mean plane of the phosphazene ring, the planes of the ligands and the planes of the dimethylamino groups, referred to the orthogonal axes $X' = ax + cz \cos \beta$, $Y' = by$, $Z' = cz \sin \beta$, are listed in Table 4. The phosphazene ring has a distorted boat form and its atoms are within -0.056 and 0.073 \AA from the mean plane as shown in detail in Fig. 3. The planes of the ligands at P(2), P(4), and P(6) make dihedral angles of 88.2 , 89.1 , and 87.1° respectively, with the mean plane of the phosphazene ring. The C(1)–N(7)–C(2) plane makes a dihedral angle of 89.2° with the plane of the ligands at P(4), while the C(3)–N(8)–C(4) and C(5)–N(9)–C(6) planes make dihedral angles of 48.0 and 45.3° , respectively, with the plane of the ligands at P(6), as can be seen from the projections given in Figs. 1 and 3. The three bonds joined at each of N(7), N(8), and N(9) are not coplanar; the mean interbond angle at each of these atoms is within $116.5 \pm 0.5^\circ$.

Table 4. Parameters of the mean planes for the normal equation $lX' + mY' + nZ' - p = 0$

	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
Phosphazene ring	0.6298	-0.6666	-0.3988	-0.6020
Cl(1), P(2), Cl(2)	-0.5485	0.0288	-0.8357	-6.9146
Cl(3), P(4), N(7)	0.2393	0.6700	-0.7027	-0.9208
N(8), P(6), N(9)	-0.7203	-0.6823	-0.1246	-5.6984
C(1), N(7), C(2)	0.4998	-0.7141	-0.4902	-2.3302
C(3), N(8), C(4)	0.3907	0.6814	-0.6189	-1.7299
C(5), N(9), C(6)	-0.7149	-0.1519	-0.6826	-9.3667

The exocyclic P(6)–N(8) and P(6)–N(9) bonds are nearly equal in length, $1.640 \pm 0.002 \text{ \AA}$, while P(4)–N(7) is only 1.628 \AA , and the difference of 0.012 \AA between them is possibly significant; $\sigma = 0.004 \text{ \AA}$ and $P = 0.02$. These three ligands are considerably shorter than the single P–N bond length of 1.77 \AA , and the P–N ligands of 1.68 \AA in $(\text{NMe}_2)_8\text{P}_4\text{N}_4$. The C–N bonds of the dimethylamino groups are between 1.452 and 1.461 \AA , and their mean is 1.455 \AA as in $(\text{NMe}_2)_8\text{P}_4\text{N}_4$.

The three P–Cl ligands have significantly different lengths of 2.014 , 1.992 , and 2.051 ($\sigma = 0.002$) \AA . The longest of these is P(4)–Cl(3) which shares atom P(4) with the shortest P–N ligand, and the shortest is P(2)–Cl(2) which is *trans* to the longest P–Cl bond.

Bond angles

In small phosphonitrilic rings, the endocyclic N–P–N angles are usually expected to be close to the trigonal value of 120° . The widest deviations from this value are observed in the N–P(C_6H_5) $_2$ –N angles of $\text{Cl}_2(\text{C}_6\text{H}_5)_4\text{P}_3\text{N}_3$ and $(\text{C}_6\text{H}_5)_2\text{Cl}_4\text{P}_3\text{N}_3$ by Mani, Ahmed & Barnes (1965, 1966), and of $(\text{C}_6\text{H}_5)_2\text{F}_4\text{P}_3\text{N}_3$ by Allen, Moeller & Paul (1969), where they occur in the range

115.2 – 115.9° . In the present structure, the N(1)–P(2)–N(3) and N(3)–P(4)–N(5) angles are 120.7 and 119.0° respectively, but the N(1)–P(6)–N(5) angle is only 113.1° . This is indicative of a more tetrahedral coordination of the bonds at P(6) than of those at P(2) and P(4). The six bond angles at P(6) vary from 103.7 to 114.2° (mean = 109.4°), while those at P(2) vary from 99.6 to 120.7° (mean = 109.1°), and the angles at P(4) vary from 104.6 to 119.0° (mean = 109.3°).

The exocyclic Cl(1)–P(2)–Cl(2) angle of 99.6° is intermediate between the corresponding values of 98.5° and 100.3° found in $\text{Cl}_2(\text{C}_6\text{H}_5)_4\text{P}_3\text{N}_3$ and $(\text{C}_6\text{H}_5)_2\text{Cl}_4\text{P}_3\text{N}_3$ respectively, but is considerably smaller than the values of 102.1° for $\text{Cl}_6\text{P}_3\text{N}_3$ by Wilson

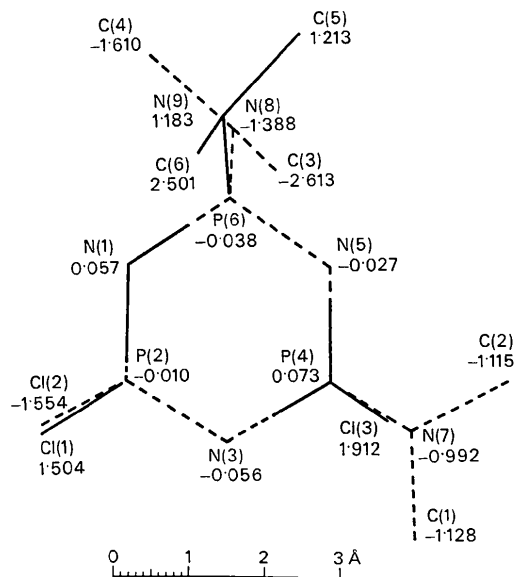


Fig. 3. Deviations (\AA) of the atoms from the mean plane of the phosphazene ring.

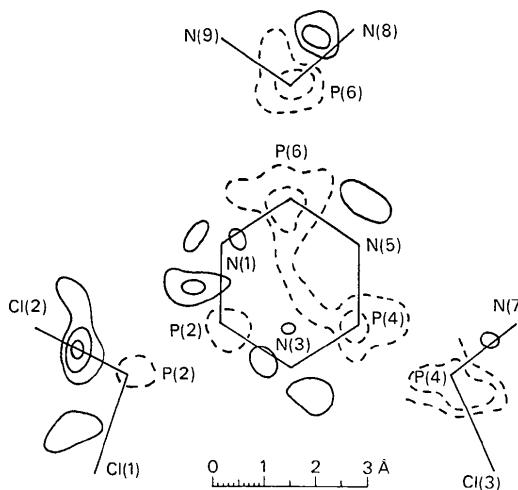


Fig. 4. Residual electron density distribution in the planes of the ring and the ligands. Contour lines start at ± 0.1 and are at intervals of $\pm 0.1 \text{ e. \AA}^{-3}$.

& Carroll (1960), and 102.8° for $\text{Cl}_8\text{P}_4\text{N}_4$ by Hazekamp, Migchelsen & Vos (1962). The exocyclic N(8)–P(6)–N(9) angle of 103.7° in this structure is comparable to the corresponding value of 103.8° in $(\text{NMe}_2)_8\text{P}_4\text{N}_4$.

Intramolecular contacts

Although there are no intermolecular contacts shorter than expected, there are four short intramolecular contacts between some of the H atoms of the methyl groups and the N atoms of the ring. These are H(7)···N(5), 2.46; H(1)···N(3), 2.55; H(6)···N(5), 2.60; and H(17)···N(1), 2.62 ($\sigma = 0.05\text{--}0.06$ Å, as identified in Fig. 1. The corresponding van der Waals contact based on the radii given by Pauling (1960) is 2.7 Å, and according to the statistics only the shortest of these contacts can be considered statistically different from the expected value. The C–H···N angles for these short contacts are 109, 106, 102, and 106° respectively.

Residual electron density

The residual electron density distribution in the mean plane of the phosphazene ring, and in the planes of the ligands is shown in Fig. 4. The positions of the P atoms have negative residual electron densities around them with troughs as low as -0.15 , -0.20 , and -0.28 e.Å $^{-3}$ at P(2), P(4), and P(6), respectively. The positions of the N atoms of the ring have positive residual electron densities of about 0.1–0.2 e.Å $^{-3}$ around them. The estimated standard deviations of the electron density is 0.08 e.Å $^{-3}$.

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Barium Aluminate Hydrates. IV. The Crystal Structure of $\alpha\text{-Ba}_2[\text{Al}_4(\text{OH})_{16}]$

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The barium aluminate hydrate $\alpha\text{-BaO}\cdot\text{Al}_2\text{O}_3\cdot 4\text{H}_2\text{O}$ has been shown by X-ray structural analysis to contain anions of formula $[\text{Al}_4(\text{OH})_{16}]^{4-}$ consisting of a cluster of four $\text{Al}(\text{OH})_6$ octahedra sharing edges. The anions are linked by the barium ions and by hydrogen bonding. The compound is thus a complex hydroxide whose formula should be written $\text{Ba}_2[\text{Al}_4(\text{OH})_{16}]$.

Introduction

The existence of a compound of empirical formula $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 4\text{H}_2\text{O}$ was first reported by Sainte-Claire-

Deville (1862). Subsequent preparations have been reported and its stability relationships have been investigated (Carlson & Wells, 1948; Carlson, Chaconas & Wells, 1950). Thilo & Gessner (1965) also prepared it; they added the prefix α to distinguish it from a different polymorph (β) which they prepared by dehydration of a higher hydrate.

The single crystals used in the present study were

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