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## Structure of *N,N*-Dimethyl-1,3,2-benzodiazaphospholium Tetrachloroaluminate: a Heteronaphthalenic 10 $\pi$ -Electron Cation

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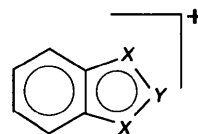
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**Abstract.** [C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>P][AlCl<sub>4</sub>],  $M_r = 333.95$ , orthorhombic, *Pbca*,  $a = 11.0690$  (5),  $b = 18.4666$  (17),  $c = 14.0975$  (12) Å,  $V = 2881.63$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.540$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.97$  mm<sup>-1</sup>,  $F(000) = 1344$ ,  $T = 293$  K,  $R = 0.055$  for 1356 significant reflections. The structure consists of discrete cationic and anionic units with long-range interactions between the P and Cl centres. The cation is planar with short P—N and C—N bond lengths [1.643 (6) and 1.379 (9) Å respectively].

**Introduction.** Isolobal derivatives of the 10 $\pi$ -electron cationic framework (1) demonstrate a constant naphthalenic environment (Burford & Royan, 1989; Burford, Royan, Linden & Cameron, 1988, 1989). The importance of this system towards the development of new bonding arrangements for the non-metal elements has been highlighted by the identification of the first examples of stable  $p\pi$  bonding between the heavier elements of Groups 15 and 16 (1*a*–*c*). The isolobal (Hoffmann, 1982; Haas, 1984) relationship between tricoordinate nitrogen and

dicoordinate sulfur has prompted a structural investigation of the title compound (1*d*). In addition, this compound is a contribution to the limited, but expanding area of dicoordinate phosphorus cations (Cowley, Cushner & Szobota, 1978; Friedrich, Huttner, Luber & Schmidpeter, 1978; Pohl, 1979; Burford *et al.*, 1988).



- (a) Y = P; X = S  
 (b) Y = As; X = S  
 (c) Y = Sb; X = S  
 (d) Y = P; X = NMe

(1)

**Experimental.** The title compound was prepared in 23% yield from the reaction of equimolar quantities of 2-chloro-1,3-dimethyl-1,3,2-benzodiazaphosphole (Jennings, Randall, Worley & Harglo, 1981) and anhydrous AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>. Pale pink air-sensitive crystals were obtained by slow evaporation of CH<sub>2</sub>Cl<sub>2</sub>. Crystal 0.58 × 0.46 × 0.23 mm (Pyrex capillary); Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation. Lattice constants were obtained from 24 well centred reflections in the range  $30 < 2\theta < 35^\circ$ . Intensities were

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Table 1. Fractional atomic coordinates with *e.s.d.*'s in parentheses and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) for the non-hydrogen atoms

$B_{\text{eq}}$  is the mean of the principal axes of the thermal ellipsoid.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
P	0.3296 (2)	0.4355 (1)	0.6928 (2)	4.4 (1)
N(1)	0.3645 (5)	0.5205 (3)	0.6742 (4)	3.7 (3)
N(2)	0.4613 (5)	0.4087 (3)	0.6509 (4)	3.8 (3)
C(1)	0.4789 (6)	0.5311 (4)	0.6383 (5)	3.5 (3)
C(2)	0.5365 (7)	0.5962 (4)	0.6145 (6)	4.2 (4)
C(3)	0.6518 (7)	0.5917 (4)	0.5779 (6)	4.7 (4)
C(4)	0.7082 (7)	0.5253 (5)	0.5644 (6)	4.6 (4)
C(5)	0.6528 (7)	0.4614 (4)	0.5866 (5)	4.3 (4)
C(6)	0.5350 (6)	0.4654 (4)	0.6240 (5)	3.6 (3)
C(7)	0.2814 (8)	0.5815 (4)	0.6926 (7)	5.3 (4)
C(8)	0.4971 (8)	0.3321 (4)	0.6435 (7)	5.7 (5)
Al	0.0128 (2)	0.3429 (1)	0.5602 (2)	4.2 (1)
Cl(1)	0.0286 (2)	0.4487 (1)	0.6176 (2)	4.7 (1)
Cl(2)	0.1628 (2)	0.2786 (1)	0.6044 (2)	6.1 (1)
Cl(3)	-0.1475 (2)	0.2941 (1)	0.6141 (2)	6.7 (1)
Cl(4)	0.0088 (3)	0.3485 (1)	0.4097 (2)	6.8 (1)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

P—N(1)	1.638 (6)	C(1)—C(2)	1.403 (10)
P—N(2)	1.648 (6)	C(2)—C(3)	1.379 (11)
N(1)—C(1)	1.378 (9)	C(3)—C(4)	1.390 (12)
N(2)—C(6)	1.380 (9)	C(4)—C(5)	1.366 (11)
N(1)—C(7)	1.477 (10)	C(5)—C(6)	1.408 (11)
N(2)—C(8)	1.474 (10)	C(1)—C(6)	1.378 (10)
Al—Cl(1)	2.138 (3)	Al—Cl(3)	2.122 (3)
Al—Cl(2)	2.125 (3)	Al—Cl(4)	2.127 (4)
N(1)—P—N(2)	91.3 (3)	P—N(1)—C(1)	114.2 (5)
P—N(1)—C(7)	123.8 (5)	C(1)—N(1)—C(7)	122.0 (6)
P—N(2)—C(6)	113.2 (5)	P—N(2)—C(8)	123.5 (5)
C(6)—N(2)—C(8)	123.3 (6)	N(1)—C(1)—C(2)	128.9 (6)
N(1)—C(1)—C(6)	110.1 (6)	C(2)—C(1)—C(6)	121.0 (7)
C(1)—C(2)—C(3)	117.3 (7)	C(2)—C(3)—C(4)	121.3 (7)
C(3)—C(4)—C(5)	122.0 (7)	C(4)—C(5)—C(6)	117.2 (7)
N(2)—C(6)—C(1)	111.1 (6)	N(2)—C(6)—C(5)	127.7 (7)
C(1)—C(6)—C(5)	121.2 (7)	Cl(1)—Al—Cl(2)	109.42 (14)
Cl(1)—Al—Cl(3)	108.49 (14)	Cl(1)—Al—Cl(4)	109.09 (13)
Cl(2)—Al—Cl(3)	108.63 (14)	Cl(2)—Al—Cl(4)	109.86 (15)
Cl(3)—Al—Cl(4)	111.33 (15)		

measured using an  $\omega/2\theta$  scan mode to  $2\theta_{\text{max}}$  of  $50^\circ$ . ( $h_{\text{max}}$  12,  $k_{\text{max}}$  21,  $l_{\text{max}}$  16). Three standard reflections monitored every hour showed no significant deviations in intensity. Intensities of 4553 reflections were measured and averaged to yield 2523 unique reflections, of which 1356 were considered observed [ $I > 2.5\sigma(I)$ ]. No absorption correction was made. The structure was solved by direct methods and refined by full-matrix least squares minimizing  $\sum w(\Delta F)^2$ , where  $w = 1/[\sigma(F)^2 + 0.00005F^2]$  and  $\sigma$  was obtained from counter statistics. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and corrected for anomalous dispersion. All non-hydrogen atoms were refined anisotropically, the H atoms were positioned at 0.96  $\text{\AA}$  from the atom to which they are attached and their isotropic thermal parameters were allowed to refine. The final cycles of refinement of 155 parameters gave  $R = 0.055$ ,  $wR = 0.059$  and a goodness of

fit of 1.62. The largest  $\Delta/\sigma$  was 0.067. A final difference synthesis showed no significant features and had a maximum of 0.42 and a minimum of  $-0.34 \text{ e \AA}^{-3}$ . All computations were performed using the PC version of *NRCVAX* (Gabe, Lee & Le Page, 1985). Table 1 lists refined fractional coordinates,\* and Table 2 provides selected bond lengths and angles. An *ORTEP* (Johnson, 1976) view of the molecular structure and a *PLUTO* (Motherwell & Clegg, 1978) stereoview of the unit-cell contents are shown in Figs. 1 and 2, respectively.

**Discussion.** The structure consists of discrete cationic and anionic units, although long-range intermolecular contacts exist between P and Cl(1) and Cl(1'), which are within the sum of the van der Waals radii.

\* Lists of structure factors, anisotropic thermal parameters, calculated planes and coordinates of calculated hydrogen positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51988 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

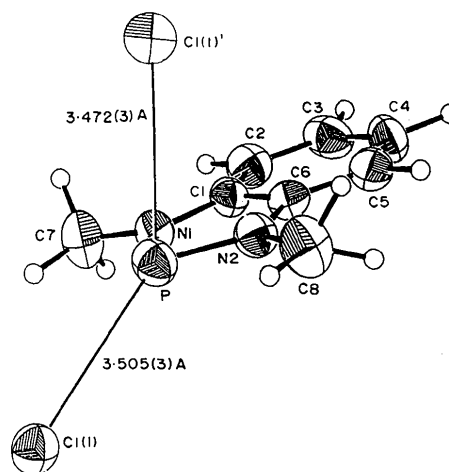


Fig. 1. *ORTEP* view of cation showing contacts which are within the sum of the van der Waals radii.

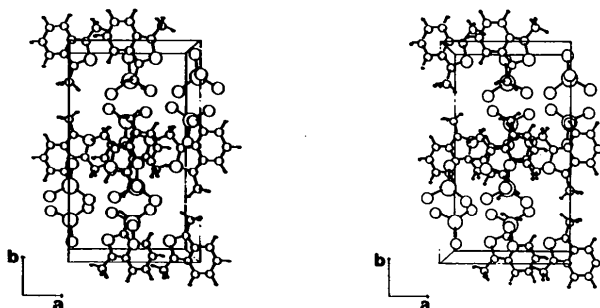


Fig. 2. Stereoview of the unit cell.

The cationic unit and the contacts are illustrated in Fig. 1 and are very similar to those observed in the structures of  $C_6H_4S_2P^+ \cdot AlCl_4^-$  (Burford *et al.*, 1988) and  $Me_2Si(N^iBu)_2P^+ \cdot AlCl_4^-$  (Veith, Bertsch & Huch, 1988). The cation is planar [maximum deviation 0.088 Å at C(7)] with P—N bond lengths [mean 1.643 (6) Å] comparable to other phosphonium cations (Cowley *et al.*, 1978; Pohl, 1979) and metallophosphonium complexes (Hutchins, Campana & Paine, 1980; Hutchins, Duesler & Paine, 1984; Hutchins, Reisacher, Wood, Duesler & Paine, 1987), indicating a substantial degree of  $p\pi-p\pi$  bonding between the P and N centres. The endocyclic C—N distances [mean 1.379 (9) Å] are significantly shorter than the exocyclic counterparts [mean 1.476 (9) Å]. The heterocyclic bond angles appear to be defined by the cyclic geometry (Hutchins *et al.*, 1980, 1984, 1987; Burford *et al.*, 1988). The molecular geometry of the benzene ring exhibits no unusual features, and the anion adopts a tetrahedral geometry comparable to that observed in other tetrachloroaluminate salts (Cardinal, Gillespie, Sawyer & Vekris, 1982).

The structural features are consistent with an efficient  $\pi$ -delocalized  $10\pi$ -electron, aromatic cation, illustrating further isolobal diversity for framework (1), while maintaining naphthalenic uniformity.

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## Structure of Dimagnesium(II) *o*-Phenylenediaminetetraacetate, [Mg<sub>2</sub>(C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>8</sub>)(H<sub>2</sub>O)<sub>6</sub>]

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**Abstract.** [Mg<sub>2</sub>(C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>8</sub>)(H<sub>2</sub>O)<sub>6</sub>],  $M_r = 493.0$ , triclinic,  $P\bar{1}$ ,  $a = 9.774$  (2),  $b = 11.466$  (1),  $c = 9.760$  (2) Å,  $\alpha = 97.25$  (1),  $\beta = 105.10$  (1),  $\gamma = 98.49$  (1)°,  $V = 1029.0$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.592$ ,  $D_x$

$= 1.591$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 17.6$  cm<sup>-1</sup>,  $F(000) = 516$ ,  $T = 298$  K,  $R = 0.035$  for 2832 observed reflections. The title compound, 1,1,1,1,1,2-hexaqua- $\mu$ -(*o*-phenylenediamine-*N,N,N',N'*-tetraacetato-*O*<sup>1</sup>:*N,N',O*<sup>2</sup>,*O*<sup>3</sup>,*O*<sup>4</sup>,*O*<sup>5</sup>)-dimagnesium(II), has a dinuclear structure, which consists of a

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