a difference synthesis. The H atom of the O···H···O bond was included without refinement at the observed position and the others were placed at calculated updated positions with $B(H)$ set at $1.2 \times B_{eq}(C)$. The secondary-extinction parameter refined to a negative value and was fixed at zero in the last cycles. Calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1989).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, intermolecular contact distances for non-H atoms, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: HA1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Salt of a Protonated (Amino)spirocyclic Cyclotriphosphazene

A. CHANDRASEKARAN†

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

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Abstract

The title compound 4,4,6,6-tetrakis(dimethylamino)-2λ⁵,4λ⁵,6λ⁵-cyclotriphosphaza-1,3,5-trien-1-ium-2-spiro-2'-(2'-phospha-1',3'-diazacyclohexane) tetra-

† Current address: Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA.

chloroplatinate, [HN₃P₃(NMe₂)₄(NHCH₂CH₂CH₂NH)]₂-[PtCl₄], contains a cyclophosphazenium cation in which the hetero-substituted (amino)spirocyclic cyclotriphosphazene is protonated. The protonation has occurred on one of the P₃N₃ ring N atoms adjacent to the spiro P atom. The protonation results in lengthening of the ring P—N bonds and puckering of the phosphazene ring. In the crystal lattice, $2n$ cyclophosphazenium cations are connected by n [PtCl₄]²⁻ anions mediated by N—H···Cl hydrogen bonds to form a linear polymeric structure.

Comment

The transition metal chemistry of cyclophosphazenes has attracted considerable interest in recent years (Allcock, Desorcie & Riding, 1987). In this context, several cyclophosphazenium salts with metal anions such as [HN₃P₃(NMe₂)₆]₂[Mo₆O₁₉] (Allcock, Bissell & Shawl, 1973), [HN₃P₃(NMe₂)₆]₂[CoCl₄] (MacDonald & Trotter, 1974), [MeN₄P₄Me₈][Cr(CO)₅I] (Calhoun & Trotter, 1974*a*), [HN₄P₄Me₈]₂[CoCl₄] (Trotter & Whitlow, 1970), [H₂N₄P₄Me₈][PtCl₄] (O'Brien, Allen & Allcock, 1979) and [H₂N₅P₅Me₁₀][CuCl₄] (Calhoun & Trotter, 1974*b*) have been studied. The protonation and coordination are found to have similar effects in altering the phosphazene-ring bond parameters and planarity. Generally the protonation occurs on the ring N atom of the amino or alkyl cyclophosphazene. In (amino)spirocyclic phosphazenes there are two kinds of N atoms in the phosphazene ring; one set adjacent to the spiro P atom and one away from it. Since no study of hetero-substituted amino or alkyl cyclophosphazenes had been carried out, the title complex, (I), was structurally characterized. The protonation has occurred on one of the N atoms adjacent to the spiro P atom which has less steric hindrance.

(I)
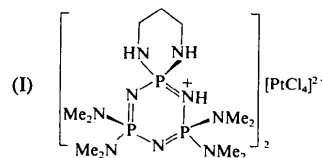
The [PtCl₄]²⁻ anion is perfectly planar as the metal lies on the crystallographic centre of inversion. All the Pt—Cl bond distances are similar. The Cl—Pt—Cl angles are not exactly 90°, a fact which can be attributed to different hydrogen-bonding interactions to the Cl atoms (see Fig. 1). There are two hydrogen bonds between the [PtCl₄]²⁻ ion and the cyclophosphazenium ion [N(1)—H(1)···Cl(1) and N(11)—H(11)···Cl(2)] which result in an eight-membered ring. As the metal lies at the centre of inversion, the other two centrosymmetrically related Cl atoms are also involved in hydrogen-bonded ring formation. Hence the metal is incorporated in two eight-membered rings resulting in discrete molecules of
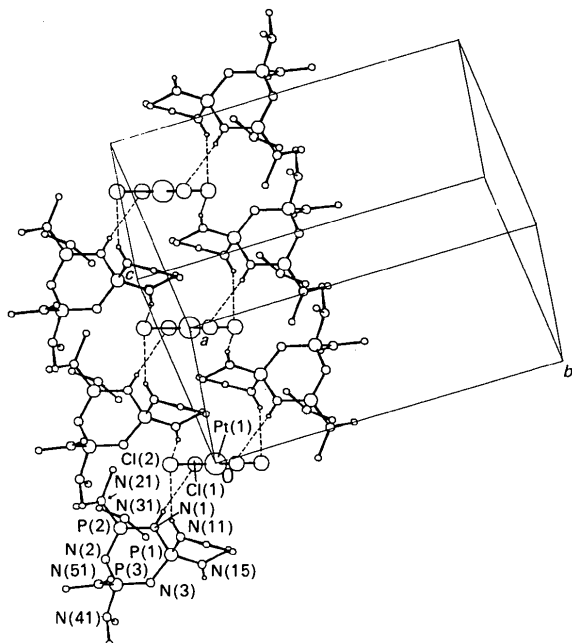
Fig. 1. Structural diagram showing the linear polymeric hydrogen-bonding network.

[HN₃P₃(NMe₂)₄(NHCH₂CH₂CH₂NH)]₂[PtCl₄]. These molecules are further connected by N(15)—H(15)···Cl(2) hydrogen bonds to give a linear polymer along the x axis. In this way, $2n$ cyclophosphazenium cations are joined by n [PtCl₄]²⁻ anions (through N—H···Cl hydrogen bonds) to form the polymeric structure.

In the phosphazenium cation, the P—N bond lengths vary significantly within the P₃N₃ ring. The bonds around the protonated N atom N(1) [1.678 (5) and 1.670 (5) Å] are longer than the remaining four ring P—N bonds [1.555 (5)–1.602 (5) Å]. Among the ring N—P—N angles, the angle at P(1) is the smallest. All the ring P—N—P angles are larger than the values normally observed for cyclophosphazene compounds. An interesting structural correlation is observed when the structures in the literature are compared. The mean ring angles at P or N fall within different ranges for cyclotriphosphazenes, their metal complexes and their protonated salts or phosphazadienes, as shown in Table 3.

The phosphazene ring (which is usually planar) is non-planar in the title compound as a result of the protonation. The protonated N atom [N(1)] deviates slightly [−0.054 (6) Å] and the P atom [P(3)] opposite to it deviates significantly [0.301 (2) Å] from the mean plane formed by the remaining four ring atoms [P(1), P(2), N(2) and N(3)]; these four atoms deviate from the plane by less than the e.s.d.'s, resulting in a distorted boat conformation. This kind of distortion from planarity upon coordination or protonation is common in cyclotriphosphazenes.

Experimental

The complex salt (I) was obtained during the attempted synthesis of the platinum chloride complex of the (amino)spirocyclic-phosphazene (by the reaction of the phosphazene with K₂PtCl₄) as a result of the presence of acid impuritites. Slow evaporation of a solution of (I) in a dichloromethane–benzene mixture led to needle-shaped cystals, which were used for the diffraction study.

Crystal data

(C₁₁H₃₃N₉P₃)₂[PtCl₄]	Mo $K\alpha$ radiation
$M_r = 1105.6$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 8.524$ (1) Å	$\theta = 9.08–15.99°$
$b = 16.607$ (2) Å	$\mu = 3.62$ mm⁻¹
$c = 16.209$ (1) Å	$T = 290$ K
$\beta = 99.66$ (1)°	Needle
$V = 2262$ Å³	$0.35 \times 0.07 \times 0.05$ mm
$Z = 2$	Brown
$D_x = 1.623$ Mg m⁻³	
$D_m = 1.628$ Mg m⁻³	
D_m measured by flotation	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.046$
diffractometer	$\theta_{max} = 25.0°$
$\omega/2\theta$ scans	$h = 0 \to 10$
Absorption correction:	$k = 0 \to 19$
refined from ΔF	$l = -19 \to 18$
(Ugozzoli, 1987)	3 standard reflections
$T_{min} = 0.662$, $T_{max} =$	frequency: 60 min
1.000	intensity variation:
4448 measured reflections	<3.91%
3970 independent reflections	
2715 observed reflections	
[$F > 6\sigma(F)$]	

Refinement

Refinement on F	$\Delta\rho_{max} = 1.86$ e Å⁻³
$R = 0.038$	$\Delta\rho_{min} = -2.17$ e Å⁻³
$wR = 0.048$	Extinction correction: none
$S = 1.578$	Atomic scattering fac-
2715 reflections	tors from SHELX76
340 parameters	(Sheldrick, 1976) and
All H-atom parameters	International Tables for
refined	X-ray Crystallography
$w = 1/\sigma^2(F_o)$	(1974, Vol. IV) for Pt
$(\Delta/\sigma)_{max} = 0.05$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	x	y	z	U_{eq}
Pt(1)	0	0	0	0.0357 (1)
Cl(1)	−0.1175 (3)	−0.0440 (1)	0.1102 (1)	0.0541 (7)
Cl(2)	0.1083 (2)	−0.1265 (1)	−0.0130 (1)	0.0540 (7)
P(1)	−0.4169 (2)	−0.1791 (1)	−0.0767 (1)	0.0300 (5)
N(1)	−0.3425 (7)	−0.1984 (3)	0.0239 (3)	0.0405 (20)
P(2)	−0.3509 (2)	−0.2848 (1)	0.0757 (1)	0.0320 (5)
N(2)	−0.4522 (7)	−0.3484 (3)	0.0199 (3)	0.0378 (20)

P(3)	−0.5043 (2)	−0.3443 (1)	−0.0797 (1)	0.0333 (6)
N(3)	−0.5108 (7)	−0.2550 (3)	−0.1155 (3)	0.0348 (20)
N(11)	−0.2633 (7)	−0.1483 (3)	−0.1140 (3)	0.0381 (22)
C(12)	−0.2699 (9)	−0.0885 (5)	−0.1821 (4)	0.0469 (25)
C(13)	−0.3825 (17)	−0.0206 (7)	−0.1755 (7)	0.1103 (60)
C(14)	−0.4657 (12)	−0.0216 (4)	−0.1019 (6)	0.0561 (32)
N(15)	−0.5306 (7)	−0.1012 (3)	−0.0897 (4)	0.0406 (20)
N(21)	−0.4161 (8)	−0.2586 (4)	0.1608 (3)	0.0438 (22)
C(22)	−0.5680 (12)	−0.2134 (7)	0.1489 (6)	0.0872 (46)
C(23)	−0.3950 (13)	−0.3139 (5)	0.2326 (5)	0.0698 (38)
N(31)	−0.1708 (8)	−0.3188 (4)	0.1090 (4)	0.0474 (22)
C(32)	−0.1157 (16)	−0.3916 (9)	0.0796 (9)	0.1316 (63)
C(33)	−0.0540 (12)	−0.2644 (6)	0.1573 (6)	0.0805 (40)
N(41)	−0.3910 (9)	−0.3983 (4)	−0.1299 (4)	0.0520 (22)
C(42)	−0.3768 (16)	−0.4855 (5)	−0.1155 (7)	0.0823 (50)
C(43)	−0.2998 (11)	−0.3685 (5)	−0.1891 (5)	0.0648 (35)
N(51)	−0.6780 (7)	−0.3895 (4)	−0.1009 (4)	0.0454 (22)
C(52)	−0.7980 (11)	−0.3637 (6)	−0.0520 (6)	0.0695 (37)
C(53)	−0.7379 (14)	−0.4070 (6)	−0.1887 (6)	0.0861 (44)

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

Pt(1)—Cl(1)	2.308 (2)	P(3)—N(3)	1.590 (5)
Pt(1)—Cl(2)	2.318 (2)	P(1)—N(11)	1.615 (6)
P(1)—N(1)	1.678 (5)	P(1)—N(15)	1.609 (6)
P(1)—N(3)	1.567 (5)	P(2)—N(21)	1.630 (6)
N(1)—P(2)	1.670 (5)	P(2)—N(31)	1.640 (7)
P(2)—N(2)	1.555 (5)	P(3)—N(41)	1.632 (8)
N(2)—P(3)	1.602 (5)	P(3)—N(51)	1.644 (6)
Cl(1)—Pt(1)—Cl(2)	90.84 (7)	N(21)—P(2)—N(31)	104.3 (3)
N(11)—P(1)—N(15)	101.8 (3)	P(2)—N(2)—P(3)	126.2 (4)
N(1)—P(1)—N(3)	108.7 (3)	N(2)—P(3)—N(3)	113.2 (3)
P(1)—N(1)—P(2)	127.7 (3)	N(41)—P(3)—N(51)	103.4 (4)
N(1)—P(2)—N(2)	111.0 (3)	P(1)—N(3)—P(3)	128.3 (3)
P(1)—N(11)—C(12)	124.1 (5)	P(1)—N(15)—C(14)	120.8 (6)

D—H···A	D—H	H···A	D···A	D—H···A
N(1)—H1···Cl(1)	0.81 (7)	2.56 (7)	3.363 (5)	172 (6)
N(11)—H11···Cl(2)	0.82 (7)	2.60 (7)	3.332 (6)	148 (6)
N(15)—H15···Cl(2i)	0.86 (7)	2.74 (8)	3.533 (7)	154 (7)

Symmetry code: (i) $x − 1, y, z$.

Table 3. *Observed trends in the ring angles* (°) *of cyclotriphosphazene derivatives*

	Cyclotriphosphazenes	Cyclotriphosphazene complexes*	Protonated salts and phosphazadienes
Mean ring N—P—N angle	119.4–116.7	116.0–114.0	112.0–110.0
Mean ring P—N—P angle	119.3–123.0	122.7–125.0	125.0–128.7
No. of structures	30	8	6

* Only when a ring N atom is involved in coordination; if it is weaker than a normal metal–nitrogen bond, the values fall within the ranges for cyclotriphosphazenes.

Data collection and cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *DRDACS* (Chandrasekaran, 1990). Structure solution (Patterson heavy-atom method) and refinement: *SHELX76* (Sheldrick, 1976). All non-H atoms were refined anisotropically; 27 of 33 H atoms were located from $\Delta\rho$ synthesis and were refined isotropically, other H atoms were not included in the calculations. Bond parameter calculations: *PARST* (Nardelli, 1983). All calculations were carried out on a VAX8810 computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances involving H atoms and bond angles involving non-H atoms have been deposited with the IUCr (Reference: AB1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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{Tris[N-(salicylidene)-2-aminoethyl]amine}cobalt(III) Acetonitrile Hemihydrate

YALCIN ELERMAN AND MEHMET KABAK

Department of Engineering Physics, Faculty of Sciences, University of Ankara, 06100 Tandogan, Ankara, Turkey

INGRID SVOBODA AND MARCUS GESELLE

Strukturforschung, FB Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstrasse 20, 64287 Darmstadt, Germany

Abstract

The slightly distorted octahedral coordination sphere of cobalt in {2,2′,2″-[nitrilotris(ethylenenitrilomethylidyne-κN)]triphenolato-$\kappa^3 O$}cobalt(III) acetonitrile hemihydrate, $[Co(C_{27}H_{27}N_4O_3)].CH_3CN.0.5H_2O$, is formed from three N and three O atoms which are in a *fac* arrangement. The chelate rings formed by the salicylidene–imine moieties are almost planar [maximum deviation of the Co atom from a least-squares