Heteroatom Chemistry
Volume 5, Number 4, 1994

Mechanism of the Controlled Hydrolysis of $(NPCl_2)_2NSOCl$: Crystal and Molecular Structure of $[KC_{12}H_{24}O_6]^+[NHPO_2NPCl_2NSOCl]^-$

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Received 22 February 1994

ABSTRACT

The reaction mechanism of controlled hydrolysis of the inorganic ring system $(NPCl_2)_2NSOCl$ *in the presence of KCl and 18-crown-6 has been revised and is explained from steric constraints rather than from electronic considerations. The X-ray structure of one of the hydrolysis products,* $[KC_{12}H_{24}O_6]^+$-$[NHPO_2NPCl_2NSOCl]^-$, *shows a dimeric structure of two centrosymmetrically related formula units kept together by hydrogen bridges and K . . . O coordination. Crystals are monoclinic, space group C2/c with* $a = 25.698(5)$, $b = 8.223(2)$, $c = 23.665(4)$ Å, $\beta = 106.03(1)^\circ$, $V = 4806(2)$ Å^3, *and* $Z = 8$. *The final R and* R_w *values are 0.048 and 0.044, respectively.*

INTRODUCTION

In a previous article [1], we reported about the controlled hydrolysis of the inorganic ring systems $(NPCl_2)_3$, $(NPCl_2)_2NSOX$, and $NPCl_2(NSOX)_2$ (X = Cl or Ph) in acetonitrile in the presence of $AsPh_4Cl$ or KCl/18-crown-6. Saltlike compounds were obtained, derived from the hydroxy derivatives of these ring systems. In addition to monosubstitution, disubstitution was also observed, which appeared to proceed via a geminal [for $(NPCl_2)_3$] and via a nongeminal substitution pattern [for $(NPCl_2)_2NSOCl$ (**1**)]. The first stage of hydrolysis of **1** showed the formation of two isomers $[KC_{12}H_{24}O_6]^+[NPCl_2NPClONSOCl]^-$ (**2**, **3**) in a ratio of 9:2. Based on the "substituent-solvating effect" [2], the anion of the most abundant isomer was assumed to have a structure in which the oxygen atoms are in the *cis* position with respect to each other. The second substitution step led to an anion with composition $[NHPO_2NPCl_2NSOCl]^-$. The tentative structure assignment was based on ^{31}P NMR data (AX-type spectrum, δ-19 and −4.6, $^2J_{PP}$ 44.6 Hz) and on IR data (absorption at 3360 cm^{-1} in $CDCl_3$ solution) [1,3].

Here, we present the crystal structure of $[KC_{12}H_{24}O_6]^+[NHPO_2NPCl_2NSOCl]^-$ (**4**), which confirms the previous structure assignment. Moreover, a new mechanism is given to explain the geminal substitution pathway during the hydrolysis of **1**.

RESULTS AND DISCUSSION

Reaction Mechanism

The first step in the hydrolysis of **1** undoubtedly leads to the formation of a *cis* and *trans* isomer of

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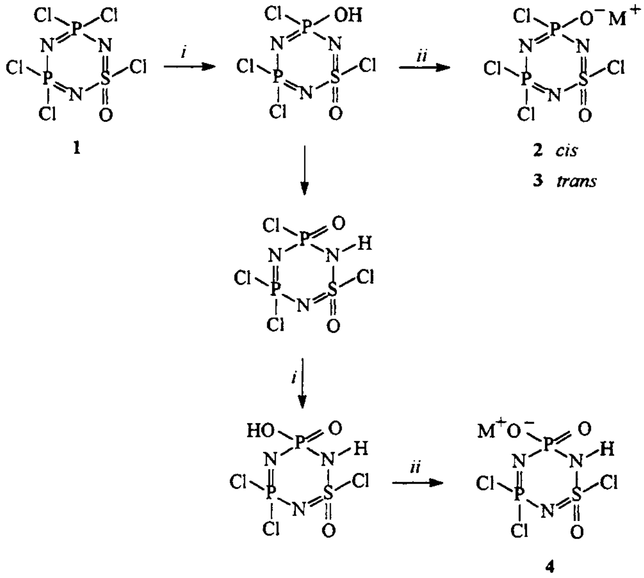


$i = H_2O$, $ii = KCl/C_{12}H_{24}O_6$, $M^+ = [KC_{12}H_{24}O_6]^+$

SCHEME 1

$NPClOHNPCl_2NSOCl$ (Scheme 1). This intermediate can react with KCl/18-crown-6 to give the isomers **2** and **3**. Hydrolysis of **2** or **3** to disubstituted products is not observed. The negative charge probably retards further nucleophilic attack.

On the other hand, tautomerization of $NPClOHNPCl_2NSOCl$ to $NHPClONPCl_2NSOCl$ explains the presence of a nitrogen-bonded hydrogen. Hydrolysis of the latter compound, followed by a reaction with K^+, leads to salt formation. From the structural data of $[Me_4N]^+[NPClO(NSOCl)_2]^-$ [4], the phosphorus-bonded oxygen ligands in $NHPOClNPCl_2NSOCl$ can be assumed to adopt equatorial positions. Therefore, the structure of the most abundant isomer, viz., *cis*-$NHPOCl$-$NPCl_2NSOCl$ probably resembles that of *cis*-$NPCl_2(NSOCl)_2$ [5]. It has been demonstrated for the dimethylaminolysis of the latter compound that, in the strongly polar solvent acetonitrile, the first substitution step does not occur at the PCl_2 center (S_N2-like) but at the SOCl center (S_N1-like) [6,7]. This phenomenon ("steric directive effect") is a consequence of the short intramolecular distances of the chlorine atoms in the *cis*-position, thus preventing the formation of an S_N2 transition state. Analogously, we presume that nucleophilic attack (S_N2) by water at the PCl_2 center of *cis*-$NHPOCl$-$NPCl_2NSOCl$ is prohibited, leading to hydrolysis at the POCl or SOCl center via an S_N1-like mechanism. As the electronegativity of phosphorus is smaller than that of sulfur, the formation of a Cl^--ion takes place at the POCl center rather than at the SOCl center. *Trans*-$NHPOClNPCl_2NSOCl$, present in very small amounts, probably decomposes during further hydrolysis. Hydrolysis of $(NPCl_2)_3$ proceeds via a nongeminal pattern. The structure of the intermediate $NHPOCl(NPCl_2)_2$ can be compared with that of **1**, in which no steric constraints, as described above, are present [8]. In conformity with this observation, aminolysis of **1** with secondary amines in acetonitrile proceeds according to a nongeminal (S_N2) pattern [9].

Structure of 4

The molecular structure of **4** can be described as cation-anion aggregates, of which the members are situated around a crystallographic inversion center (Figure 1).

Two NPS ring systems form a dimer interconnected via N–H . . . N hydrogen bonds, viz., N(1)–H(1) . . . N(2a) and the symmetrically related N(1a)–H(1a) . . . N(2). The H(1) . . . N(2a) distance amounts to 2.27(5) Å (sum of the van der Waals radii is 2.75 Å). The angle N(1)–H(1) . . . N(2a) is 165(4)°. In two related, but neutral, compounds $NHP(O)Me$-$NP(OMe)_2NPPh_2$ and $NHP(O)NEt_2NPCl_2NP(NEt_2)_2$, the dimers are kept together by N–H . . . O = P hydrogen bonding [10]. A second bonding interaction is caused by the coordination of the potassium cation towards six oxygen atoms of an 18-crown-6 group [K(1) . . . O varying from 2.851(3) to 3.053(3) Å; sum of the van der Waals radii 3.65 Å] and towards O(1) and O(2a) [K(1) . . . O(1) = 2.783(3), K(1) . . . O(2a) = 2.868 Å], each belonging to two different ring systems. For symmetry reasons, the aggregate is completed by a second 18-crown-6 group with coordination of K(1a) towards crown ether oxygens and toward O(2) and O(1a). The potassium cation is located at 0.94(1) Å from the least-squares mean plane of the six crown ether oxygens.

The 18-crown-6 molecular conformation has approximate D_{3d} symmetry, which is found in most complexes of the crown ether compound [11]. The C–O bond lengths are alternating short and long, probably due to some disorder of the crown ring (Table 1). The average C–C distance amounts to 1.469(6) Å.

The conformation of the inorganic ring can be described as an envelope [12]. Puckering parameters are $Q = 0.509$ Å, $\theta = 127.7(3)°$ and $\varphi = 305.7(4)°$. The atom P(1) is tilted by 0.71(3) Å from the least-squares plane through the atoms S(1), P(2), N(1), N(2), and N(3). Comparison of the bond lengths and angles of **4** with those of its precursor $(NPCl_2)_2NSOCl$ (**1**) [8] reveals several interesting features (Figure 2).

The presence of a hydrogen-substituted endocyclic nitrogen, N(1), exerts a substantial influence on the bonding properties of the PNS ring. In the ring segment P(1)N(1)S(1), both the N–S and N–P bond distances [mean value 1.682(4) Å] are consid-

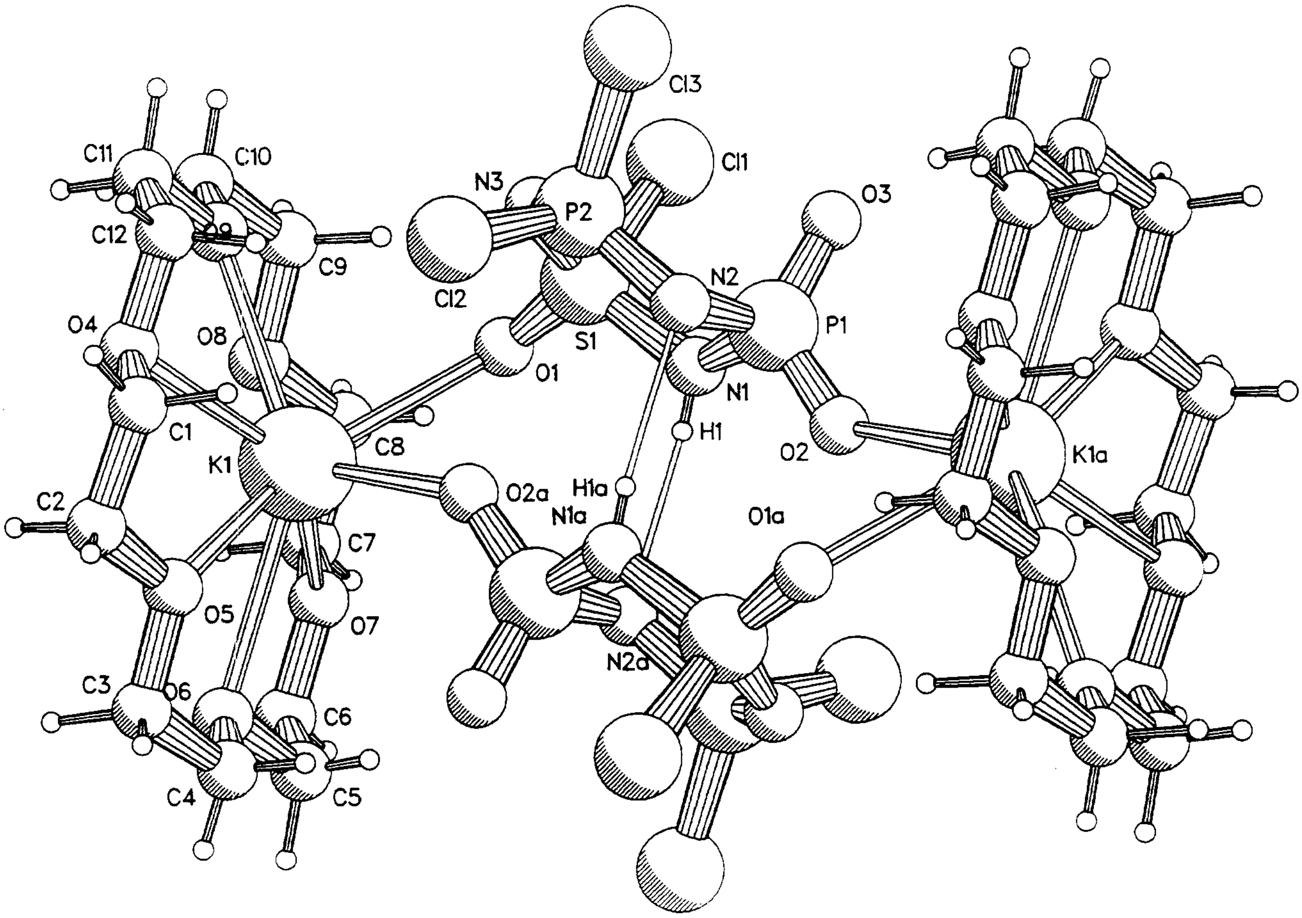


FIGURE 1 PLUTO drawing of the cation-anion aggregate of **4** together with the adopted numbering scheme.

erably longer than those found in **1** [N–S = 1.557(2), N–P = 1.606(2) Å (mean values)]. This points to a decrease of the d_π-p_π character of the PN(H)S segment, resulting in a phosphazane moiety. In the segment P(1)N(2)P(2), the bond lengths are equal within the experimental error. This indicates that, in the present anion, the electronegativity of the phosphorus centers is of the same magnitude. Differences in bond lengths in the segment S(1)N(3)P(2) are larger, although hardly significant. The presence of two P-bonded oxygens results in a widening of the O–P–O angle in comparison with the Cl–P–Cl angle; the corresponding N–P–N angle is smaller, 106.5(2) vs. 118.2(2)° (Figure 2). Only one of the P-bonded oxygen ligands, viz., O(2), coordinates to a potassium cation. Surprisingly, both P–O bond lengths are equal. Coordination of the S-bonded oxygen ligand O(1) towards potassium results in lengthening of the S–O bond [1.464(3) Å vs. 1.422(3) Å in **1**]. The smaller distance of K ... O(1) [2.783(3) Å] compared with K(1a) ... O(2) [2.868(3) Å] leads to the conclusion that a considerable amount of the negative charge is transferred from the phosphorus to the sulfur center.

EXPERIMENTAL

Synthesis

Compound **4** was synthesized by hydrolysis of two equivalents of water in the presence of KCl and 18-crown-6, using acetonitrile as solvent. Details with respect to purification and spectroscopic (NMR, IR) identification are given in Ref. [1].

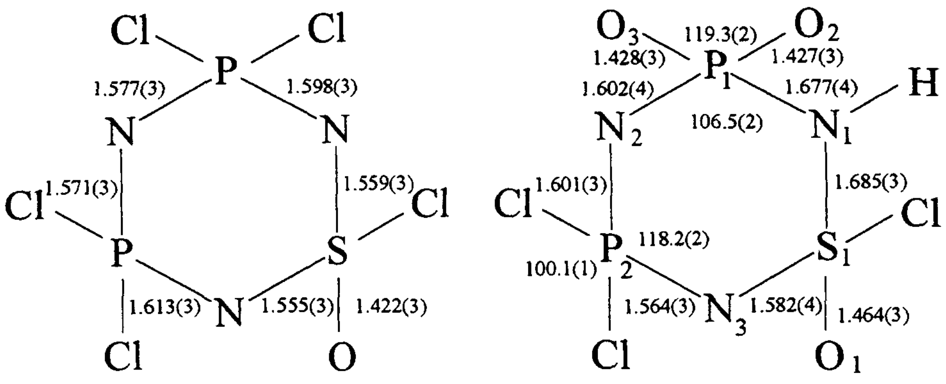
Structure Determination of 4

A suitable, colorless crystal (dimensions 0.08 × 0.31 × 0.33 mm) of **4** obtained by recrystallization from a 1:3 mixture of CH_2Cl_2 and Et_2O was glued on the top of a glass fiber and mounted on an Enraf–Nonius CAD-4F diffractometer. Lattice constants and their standard deviations were determined from the setting angles of 22 reflections in the range $21 < \theta < 22°$. The space group was derived from the observed systematic absences as C2/c or Cc. The former was chosen and confirmed by a successful refinement in this space group. Intensity data for 7688 reflections were collected at 100 K in the range of $0.9 < \theta < 24.5°$, using graphite-monochromated Mo K_α radiation and the ω-2θ technique, with ω scan

TABLE 1 Selected Data on the Geometry of **4** with Esd's in Parentheses

Bond Distances (Å)					
PNS Ring Anion					
S(1)–N(1)	1.685(3)	P(2)–N(3)	1.564(3)	P(1)–O(2)	1.427(3)
S(1)–N(3)	1.582(4)	S(1)–Cl(1)	2.032(2)	P(1)–O(3)	1.428(3)
P(1)–N(1)	1.677(4)	P(2)–Cl(2)	1.988(2)	N(1)–H(1)	0.78(5)
P(1)–N(2)	1.602(4)	P(2)–Cl(3)	2.024(2)		
P(2)–N(2)	1.601(3)	S(1)–O(1)	1.464(3)		
18-crown-6					
O(4)–C(1)	1.444(6)	O(7)–C(6)	1.405(6)	C(1)–C(2)	1.476(7)
O(4)–C(12)	1.404(6)	O(7)–C(7)	1.439(6)	C(3)–C(4)	1.496(8)
O(5)–C(2)	1.387(7)	O(8)–C(8)	1.405(6)	C(5)–C(6)	1.450(7)
O(5)–C(3)	1.451(6)	O(8)–C(9)	1.434(6)	C(7)–C(8)	1.466(7)
O(6)–C(4)	1.395(6)	O(9)–C(10)	1.399(6)	C(9)–C(10)	1.465(8)
O(6)–C(5)	1.438(6)	O(9)–C(11)	1.440(6)	C(11)–C(12)	1.467(7)
Coordination Distances					
K . . . O(1)	2.783(3)	K ... O(6)	3.043(3)		
K . . . O(2a)	2.868(3)	K ... O(7)	2.851(3)		
K . . . O(4)	2.909(3)	K ... O(8)	3.053(3)		
K . . . O(5)	2.912(3)	K ... O(9)	2.864(3)		
Bond Angles (°)					
PNS Ring Anion					
N(1)–S(1)–N(3)	110.5(2)	Cl(1)–S(1)–O(1)	108.6(1)		
N(1)–P(1)–N(2)	106.5(2)	O(2)–P(1)–O(3)	119.3(2)		
N(2)–P(2)–N(3)	118.2(2)	Cl(2)–P(2)–Cl(3)	100.1(1)		
S(1)–N(1)–P(1)	118.7(3)				
P(1)–N(2)–P(2)	114.6(2)				
S(1)–N(3)–P(2)	125.5(2)				
18-crown-6					
Mean value C–O–C	112.6(3)			mean value O–C–C	109.4(2)

Hydrogen bond N(1)–H(1) . . . N(2a)
N(1)–H(1) 0.75(5) Å H(1) . . . N(2a) 2.27(5) Å N(1)–H(1) . . . N(2a) 165(4)°



1 **4**

FIGURE 2 Comparison of the bond lengths and angles of **1** and **4**.

width = (0.80 + 0.35 tg θ). Three reference reflections measured every 2 hours showed a long-term variation of less than 2% during the 56.4 hours of X-ray exposure time. A 360° ψ-scan for the reflection 020 showed a variation in intensity of less than 7% of the mean value. The intensities were corrected for scale variation and Lorentz and polarization effects. Absorption correction was applied with DIFABS [13]. The variance $\sigma^2(I)$ was calculated based on counting statistics plus a term $(PI)^2$, where P (=0.0139) is the instability constant [14]. The data set was averaged to a set of 3852 unique reflections satisfying the $I \geq 2.5\sigma$ criterion of observability. The structure was solved by direct methods using GENTAN [15] and refined on F by block-diagonal least-squares with anisotropic thermal parameters for the nonhydrogen atoms. Hydrogen atoms located on a difference Fourier map were included in the final refinement with one overall isotropic temperature factor. Convergence was reached at $R = 0.048$ and $R_w = 0.044$. Final fractional atomic coordinates and isotropic thermal parameters for the nonhydrogen atoms are given in Table 2. Scattering factors were taken from Cromer and Mann [16], and anomalous dispersion factors were from Cromer and Liberman [17]. All calculations were carried out on the Cyber 180–855 of the University of Utrecht Computer Center, with the programs XTAL [15], EUCLID [18], and a locally modified version of PLUTO [19].

TABLE 2 Atomic Coordinates and Isotropic Thermal Parameters for Non-H Atoms of **4** with Esd's in Parentheses.

	x	y	z	U_{eq} (Å^2)^a
K(1)	0.34322(5)	0.67490(14)	−0.13692(5)	0.0296(4)
Cl(1)	0.35349(5)	0.33010(16)	0.06804(5)	0.0246(4)
Cl(2)	0.46638(5)	0.93056(16)	0.05410(6)	0.0295(4)
Cl(3)	0.45506(5)	0.75969(18)	0.16568(6)	0.0358(5)
S(1)	0.38849(4)	0.46697(15)	0.01706(5)	0.0193(4)
P(1)	0.50024(4)	0.41253(15)	0.08169(5)	0.0150(4)
P(2)	0.45546(5)	0.70867(15)	0.08211(5)	0.0197(4)
O(1)	0.35466(11)	0.4586(4)	−0.4379(12)	0.019(1)
O(2)	0.54581(12)	0.3395(4)	0.06833(13)	0.0254(11)
O(3)	0.48516(12)	1.3599(4)	0.13250(13)	0.0260(11)
O(4)	0.33380(13)	0.0199(4)	−0.11430(14)	0.0270(11)
O(5)	0.39825(13)	0.9224(4)	−0.18716(14)	0.0287(11)
O(6)	0.36590(13)	0.6497(4)	−0.25621(14)	0.0277(11)
O(7)	0.30144(14)	0.4202(4)	−0.21864(13)	0.0284(11)
O(8)	0.23126(12)	0.5274(4)	−0.15115(13)	0.0245(11)
O(9)	0.26695(12)	0.7945(4)	−0.07859(13)	0.0251(11)
N(1)	0.44753(14)	0.3691(5)	0.02391(15)	0.0152(12)
N(2)	0.50816(14)	0.6057(5)	0.08160(15)	0.0178(12)
N(3)	0.39877(14)	0.6381(5)	0.04876(17)	0.0209(12)
C(1)	0.3850(2)	1.0934(7)	−0.1136(2)	0.0368(19)
C(2)	0.3923(2)	1.0840(7)	−0.1732(2)	0.0348(17)
C(3)	0.4098(2)	0.9046(7)	−0.2435(2)	0.0375(19)
C(4)	0.41431(19)	0.7274(7)	−0.2557(2)	0.0325(19)
C(5)	0.3656(2)	0.4790(6)	−0.2695(2)	0.0310(17)
C(6)	0.3129(2)	0.4096(6)	−0.2732(2)	0.0319(19)
C(7)	0.2504(2)	0.3467(6)	−0.2193(2)	0.0278(17)
C(8)	0.2402(2)	0.3629(6)	−0.1616(2)	0.0292(17)
C(9)	0.21958(19)	0.5503(7)	−0.0959(2)	0.0293(19)
C(10)	0.21636(19)	0.7240(7)	−0.0837(2)	0.0279(19)
C(11)	0.2688(2)	0.9652(6)	−0.0646(2)	0.0275(17)
C(12)	0.3235(2)	1.0279(6)	−0.0591(2)	0.0311(17)

$^aU_{eq} = 1/3\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i \cdot \mathbf{a}_j$

ACKNOWLEDGMENTS

This investigation was supported in part (HW, ALS) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research. The authors are indebted to Dr. J. L. de Boer for collecting the X-ray data.

SUPPLEMENTARY MATERIAL AVAILABLE

Summaries of the structure determination of **4**, including tables of crystal data, atomic coordinates and equivalent isotropic thermal displacement parameters, (an)isotropic thermal displacement coefficients, bond distances, bond angles, torsion angles, and observed and calculated structure factors are available. These data may be obtained by request to the authors.

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