

The Crystal Structure of the 1:1 Compound between Ammonium *P,P*-Dithiophosphacyanurate and Urea

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The structure of a 1:1 compound between ammonium *P,P*-dithiophosphacyanurate and urea has been solved by direct methods and refined by full-matrix least-squares calculations to a final *R* of 0.029 for 1891 observed reflexions. The structure is triclinic, space group $P\bar{1}$, with $a = 5.0187$ (2), $b = 9.9219$ (3), $c = 11.9417$ (5) Å, $\alpha = 71.108$ (6), $\beta = 85.529$ (7), $\gamma = 81.222$ (13)°, $Z = 2$, and consists of urea molecules, ammonium ions and cyclic anions with the formula $C_2H_3N_3O_2PS_2^-$. The anions contain a non-planar 6-membered ring C_2N_3P . The S and O atoms in the anions are acceptors of hydrogen bonds, linking the different moieties into a three-dimensional network.

Introduction

Several compounds are formed when urea and phosphorus pentasulphide are allowed to react at 100°C and the product then treated with water. Hemmelmayr (1905) proposed that the first substance to crystallize on evaporation is either $C_2H_7N_4O_2PS_2$ (I) or $C_2H_7N_4O_2PS_2 \cdot x(NH_2)_2CO$ (II).

An investigation (Aurivillius & Stålhandske, 1975) has confirmed the empirical and structural formula of (I), named ammonium *P,P*-dithiophosphacyanurate. Repeating Hemmelmayr's synthesis we have found that in some cases a triclinic phase is formed as well as the monoclinic substance (I). Triclinic crystals with identical powder photographs were also obtained as the first crystallization product from water solutions containing (I) and urea in the molar ratio 1:*n*, $n > 10$. It thus seems probable that the triclinic substance is the one denoted (II) with the empirical formula $C_2H_7N_4O_2PS_2 \cdot x(NH_2)_2CO$; the present study was initiated to elucidate its composition and structure.

Experimental

An Enraf-Nonius computer-controlled four-circle diffractometer equipped with a graphite monochromator and Cu $K\alpha$ radiation was used to collect X-ray inten-

sities for (II) from a prismatic single crystal of volume 0.0019 mm³.

The θ values of 45 reflexions were measured on the diffractometer and the dimensions of the triclinic unit cell calculated by least squares. Some crystal data are given in Table 1.

The intensities of 2076 unique reflexions were measured with the ω - 2θ scan technique and a scan interval $\Delta\omega = 0.90 + 0.50 \tan \theta$. Of these reflexions, 185 with $I < 3\sigma(I)$, where $\sigma(I)$ was based on counting statistics, were considered unobserved. The intensities of three control reflexions showed a linear decay of 2.5%. All measured intensities and their variances, scaled for this decrease, were corrected for Lorentz, polarization and absorption effects. The transmission factors varied from 0.46 to 0.66.

Determination and refinement of the structure

Space group $P\bar{1}$ was assumed as centrosymmetry was indicated by $|E|$ statistics. Symbolic addition was performed and one of the *E* maps revealed most of the non-hydrogen atoms. Remaining atoms, including H, were found by successive least-squares and difference electron density calculations.

The final full-matrix least-squares refinement included anisotropic temperature factors for the non-hydrogen and isotropic for the H atoms. A parameter to correct for isotropic secondary extinction was also refined (Zachariasen, 1967). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|^2)/4|F_o|^2 + 0.0003|F_o|^2 + 0.30$. The resulting $R = (|F_o| - |F_c|)/\sum |F_o| = 0.029$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.041$. The goodness of fit, $S = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, where m and n are the number of observations and parameters varied, respectively, was 1.5. The extinction parameter $g = 1.3(1) \times 10^2$. Scattering factors for the non-hydrogen atoms were taken from Doyle & Turner

Table 1. *Crystal data*

Formula	$NH_4^+(C_2H_3N_3O_2PS_2)^- \cdot (NH_2)_2CO$
F.W.	274.26
	$a = 5.0187$ (2) Å $\alpha = 71.108$ (6)°
	$b = 9.9219$ (3) $\beta = 85.529$ (7)
	$c = 11.9417$ (5) $\gamma = 81.222$ (13)
	$V = 555.76$ Å ³ , $T = 295$ K
Space group	$P\bar{1}$ (No. 2)
	$D_m = 1.62$, $D_x = 1.64$ g cm ⁻³
<i>Z</i>	2
μ (Cu $K\alpha$)	55.5 cm ⁻¹

Table 2. Positional parameters and isotropic temperature factors

B denotes the isotropic temperature factor. For labelling of the atoms, cf. Fig. 2. The estimated standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
S(1)	0.44417 (13)	0.86886 (7)	0.44014 (6)	For β_{ij}
S(2)	0.11582 (12)	0.91038 (6)	0.19532 (5)	and r.m.s.
P	0.35055 (10)	0.78385 (6)	0.32492 (5)	com-
O(1)	0.8221 (4)	0.5637 (3)	0.1606 (2)	ponents
O(2)	0.1087 (4)	0.4155 (2)	0.3955 (2)	see
O(3)	0.4912 (4)	0.2678 (3)	0.1864 (2)	Table 3.
N(1)	0.6286 (4)	0.7084 (3)	0.2665 (3)	
N(2)	0.4381 (4)	0.5092 (3)	0.2664 (3)	
N(3)	0.2237 (5)	0.6283 (3)	0.3942 (2)	
N(4)	0.0283 (6)	0.1772 (3)	0.3239 (3)	
N(5)	0.7912 (6)	0.3429 (3)	0.0397 (3)	
N(6)	0.5550 (6)	0.1609 (3)	0.0460 (3)	
C(1)	0.6414 (5)	0.5938 (3)	0.2268 (3)	
C(2)	0.2474 (5)	0.5131 (3)	0.3549 (2)	
C(3)	0.6071 (5)	0.2580 (3)	0.0928 (3)	
H(1)	0.755 (6)	0.753 (4)	0.243 (3)	3 (1)
H(2)	0.447 (6)	0.440 (4)	0.240 (3)	3 (1)
H(3)	0.114 (6)	0.627 (3)	0.448 (3)	2 (1)
H(41)	0.062 (11)	0.257 (7)	0.364 (5)	11 (2)
H(42)	0.085 (9)	0.094 (5)	0.367 (4)	7 (2)
H(43)	-0.135 (13)	0.206 (6)	0.298 (5)	10 (2)
H(44)	0.131 (10)	0.204 (6)	0.264 (5)	9 (2)
H(51)	0.868 (7)	0.334 (4)	-0.016 (4)	5 (1)
H(52)	0.818 (7)	0.408 (4)	0.076 (4)	5 (1)
H(61)	0.634 (7)	0.150 (4)	-0.008 (4)	5 (1)
H(62)	0.434 (7)	0.104 (4)	0.083 (4)	5 (2)

(1968) and for H from Stewart, Davidson & Simpson (1965). The final coordinates and isotropic temperature factors are given in Table 2* and the anisotropic thermal parameters with r.m.s. components in Table 3. An account of the programs has been given (Stålhandske, 1974).

Description and discussion of the structure

The structure is built up of cyclic anions with the formula $C_2H_3N_3O_2PS_2^-$, ammonium ions and urea molecules. A stereoscopic view of the contents of one unit cell is given in Fig. 1. Selected distances and angles in the structure are given in Figs. 2, 3 and Table 4.

The anion $C_2H_3N_3O_2PS_2^-$, which was first shown to exist in ammonium *P,P*-dithiophosphacyanurate(I) (Aurivillius & Stålhandske, 1975), contains a non-planar ring C_2N_3P . The anion may be regarded as a cyanuric acid molecule ($C_3H_3N_3O_3$) where one CO is replaced by PS_2^- . Distances and angles in the anion (Fig. 2 and Table 4) are in good agreement with the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31260 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Anisotropic thermal parameters and r.m.s. components

The expression for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The estimated standard deviations are given in parentheses. The β_{ij} values are $\times 10^4$ and r.m.s. components $\times 10^3$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1 (Å)	R_2 (Å)	R_3 (Å)
S(1)	391 (4)	93 (2)	63 (1)	-32 (2)	-15 (2)	-47 (1)	146 (1)	220 (2)	225 (2)
S(2)	265 (3)	68 (1)	51 (1)	-37 (2)	5 (2)	-19 (1)	162 (1)	180 (1)	190 (2)
P	210 (3)	56 (1)	43 (1)	-32 (2)	19 (1)	-25 (1)	137 (2)	146 (2)	186 (2)
O(1)	265 (7)	104 (3)	66 (2)	-39 (4)	52 (3)	-42 (2)	144 (3)	197 (3)	238 (3)
O(2)	360 (8)	65 (2)	52 (2)	-58 (3)	45 (3)	-24 (2)	152 (3)	163 (3)	235 (3)
O(3)	524 (10)	106 (3)	71 (2)	-110 (4)	100 (4)	-49 (2)	156 (3)	182 (3)	300 (3)
N(1)	193 (8)	82 (3)	72 (2)	-48 (4)	34 (3)	-38 (2)	138 (4)	170 (3)	229 (3)
N(2)	276 (9)	72 (3)	56 (2)	-41 (4)	35 (4)	-37 (2)	142 (4)	165 (4)	220 (3)
N(3)	291 (9)	66 (3)	47 (2)	-40 (4)	48 (4)	-25 (2)	137 (4)	162 (3)	221 (3)
N(4)	445 (13)	91 (3)	74 (2)	-50 (5)	41 (5)	-41 (3)	176 (3)	202 (4)	257 (4)
N(5)	507 (13)	143 (4)	82 (3)	-124 (6)	113 (5)	-57 (3)	158 (4)	216 (4)	312 (4)
N(6)	513 (13)	111 (4)	64 (3)	-67 (6)	50 (4)	-45 (2)	169 (4)	210 (4)	271 (4)
C(1)	212 (9)	74 (3)	48 (2)	-15 (4)	9 (3)	-23 (2)	156 (4)	177 (4)	184 (3)
C(2)	251 (9)	59 (3)	42 (2)	-21 (4)	7 (3)	-16 (2)	159 (4)	163 (4)	182 (4)
C(3)	339 (11)	81 (3)	53 (2)	-18 (5)	27 (4)	-25 (3)	164 (4)	190 (4)	221 (4)

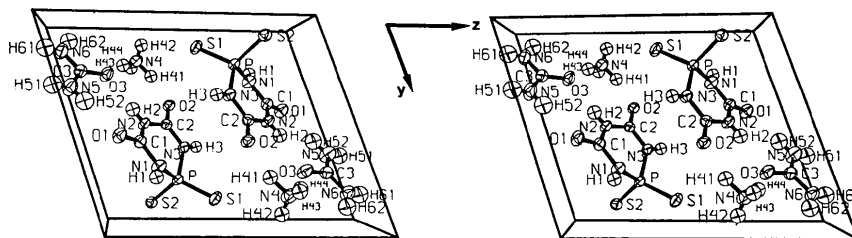


Fig. 1. A stereoscopic view of one unit cell of the structure. The thermal ellipsoids are drawn to enclose 50% probability. The ammonium H atoms are drawn with temperature factors of 3 \AA^2 .

Table 4. Selected distances (Å) and angles (°)

Estimated standard deviations are given in parentheses

Ammonium ion

N(4)–H(41)	1.10 (6)	H(41)–N(4)–H(42)	111 (5)
N(4)–H(42)	0.84 (5)	H(41)–N(4)–H(43)	104 (5)
N(4)–H(43)	0.87 (6)	H(41)–N(4)–H(44)	97 (5)
N(4)–H(44)	0.84 (6)	H(42)–N(4)–H(43)	125 (5)
		H(42)–N(4)–H(44)	111 (5)
		H(43)–N(4)–H(44)	105 (5)

Angles at the P atom

S(1)–P–N(1)	111.5 (1)
S(1)–P–N(3)	110.5 (1)
S(2)–P–N(1)	109.4 (1)
S(2)–P–N(3)	111.0 (1)
S(1)–P–S(2)	116.6 (1)

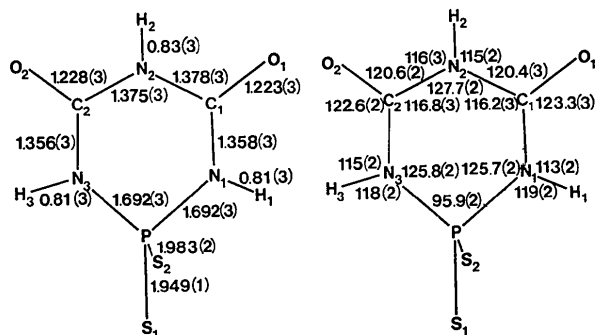
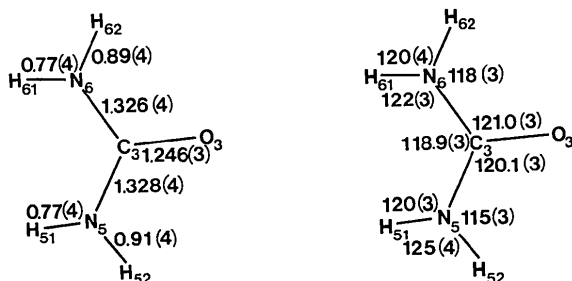
Fig. 2. Distances (Å) and angles (°) in the anion $C_2H_3N_3O_2PS_2^-$. Estimated standard deviations are given in parentheses. The S–P–N and S–P–S angles are listed in Table 4.

Fig. 3. Distances (Å) and angles (°) in the urea molecule. Estimated standard deviations are given in parentheses.

corresponding values found in (I) except for the C(2)–N(2) distance of 1.375 (3) Å which was 1.390 (2) Å in (I). The anions in the present structure and in (I) were compared by half-normal probability plots (Abrahams & Keve, 1971; De Camp, 1973), which indicated that the e.s.d.'s are underestimated by a factor of 2. No differences in distances and angles in the anions are then significant. The non-hydrogen atoms of the two urea parts of the anion [N(1), C(1), O(1), N(2) and N(3), C(2), O(2), N(2)] are almost planar (Table 5). The two parts form a dihedral angle of 169.0 (5)°.

Table 5. Least-squares planes

Distances from the planes (Å) are $\times 10^3$. Atoms used to define the planes are marked with asterisks.

Plane I	Plane II	Plane III
N(1)* 1	N(3)* 1	N(5)* 3
C(1)* -4	C(2)* -2	C(3)* -9
O(1)* 1	O(2)* 1	O(3)* 3
N(2)* 1	N(2)* 1	N(6)* 3
P -433	P -354	H(51) 31
H(1) 27	H(3) 23	H(52) -12
C(2) 217	C(1) 246	H(61) 59
H(2) -17	H(2) -38	H(62) 10

The P atom is roughly tetrahedrally coordinated to two N and two S atoms. The P–N distances are both 1.692 (3) Å and indicate some π -bond character as the length of a P–N single bond is 1.77 Å (Pauling, 1960). This shortening can be explained by a delocalization of the lone pair of electrons from the N atom into a vacant 3d orbital of P. The two P–S distances, 1.949 (1) and 1.983 (2) Å lying between the values 1.94 and 2.14 Å given by Pauling (1960) for a P–S double and single bond, are compared with P–S distances in other dithiophosphates in Table 6.

H(41)–H(44) of the ammonium group have large thermal motions, resulting in low accuracy in their positions. The N–H distances vary between 0.84 and 1.10 Å and the H–N–H angles between 97 and 125° (Table 4).

Distances and angles in the urea molecule are shown in Fig. 3. The C=O length 1.246 (3) Å and the C–N distances of 1.326 (4) and 1.328 (4) Å are somewhat shorter than the corresponding values, without correction for librational motion, given by Pryor & Sanger (1970) from a neutron diffraction study. The distances

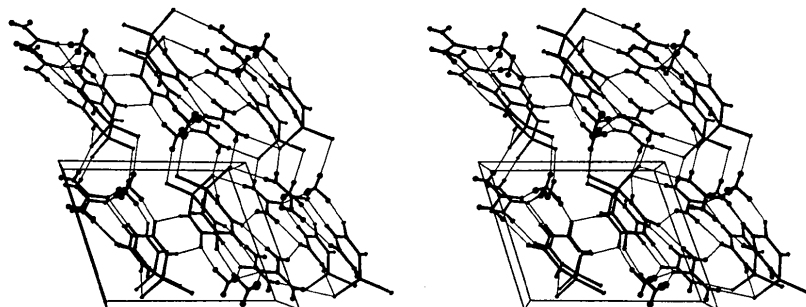


Fig. 4. Stereoscopic illustration of the hydrogen bonding. The hydrogen bonds are drawn with thin lines.

Table 6. Comparison of P-S bond lengths and S-P-S bond angles in selected dithiophosphates

	Short distance P-S	Long distance P-S	Average P-S	Angle S-P-S	References
NH ₄ (C ₂ H ₃ N ₃ PO ₂ S ₂)·(NH ₂) ₂ CO	1·949 (1)	1·983 (2)	1·97	116·6 (1)	This work
NH ₄ (C ₂ H ₃ N ₃ PO ₂ S ₂)	1·953 (1)	1·987 (1)	1·97	116·0 (1)	Aurivillius & Stålhandske (1975)
K[S ₂ P(OCH ₃) ₂]	1·960 (13)	1·960 (13)	1·96	118·2 (9)	Coppens, MacGillavry, Hovenkamp & Douwes (1962)
Zn[S ₂ P(OC ₂ H ₅) ₂] ₂	1·973 (11) 1·992 (7)	1·987 (9) 2·001 (5)	1·99	109·7 (4) 108·0 (3)	Ito, Igarashi & Hagihara (1969)
Pb[S ₂ P(OC ₂ H ₅) ₂] ₂	1·968 (7) 1·969 (7)	1·991 (9) 1·995 (8)	1·98	116·2 (4) 115·4 (3)	Ito (1972)
Pb[S ₂ P(i-OC ₃ H ₇) ₂] ₂	1·93 1·95	1·99 2·03	1·98		Lawton & Kokotailo (1969)

Table 7. Distances (Å) and angles (°) in hydrogen bonds

A-H···B	A-H	A···B	H···B	∠A-H···B
N(1)-H(1)···S(2)	0·81 (3)	3·285 (3)	2·48 (3)	171 (3)
N(2)-H(2)···O(3)	0·83 (3)	2·821 (3)	1·99 (4)	176 (3)
N(3)-H(3)···O(2)	0·81 (3)	2·853 (3)	2·06 (3)	167 (3)
N(4)-H(41)···O(2)	1·10 (6)	2·854 (4)	1·78 (6)	167 (5)
N(4)-H(42)···S(1)	0·84 (5)	3·376 (3)	2·60 (5)	154 (4)
N(4)-H(43)···O(3)	0·87 (6)	3·124 (4)	2·28 (7)	165 (5)
N(4)-H(44)···O(3)	0·84 (6)	2·826 (4)	2·06 (6)	152 (5)
N(5)-H(51)···O(1)	0·77 (4)	2·956 (4)	2·31 (4)	142 (4)
N(5)-H(52)···O(1)	0·91 (4)	3·015 (4)	2·11 (4)	172 (4)
N(6)-H(61)···S(2)	0·77 (4)	3·428 (3)	2·67 (4)	174 (4)
N(6)-H(62)···S(2)	0·89 (4)	3·522 (3)	2·64 (4)	174 (3)

are also shorter than those reported from various refinements of urea based on X-ray data (Vaughan & Donohue, 1952; Caron & Donohue, 1964; Pryor & Sanger, 1970). On the other hand the present values agree well with those given by Mahmoud & Wallwork (1975) in the 1:1 complex between quinol and urea, where C=O is 1·253 (2) Å and C-N 1·332 (3) and 1·335 (3) Å.

The angles involving the non-hydrogen atoms of the urea molecule are in good agreement with those reported in the neutron and X-ray studies mentioned above. The largest deviation from the best plane through the atoms C, N and O of the urea molecule (Table 5) is for the non-hydrogen atoms 0·009 Å [C(3)] and for the H atoms 0·059 Å [H(61)].

The proposed hydrogen bonding is presented in a stereoscopic drawing (Fig. 4) and in Table 7. The sums of the van der Waals radii are used as upper limits for the H···O, H···N and H···S acceptor distances, 2·4, 2·5 and 2·7 Å, respectively. In the hydrogen bonds the N atoms are the only donors and O and S atoms the acceptors. The different moieties of the structure are linked by hydrogen bonds into layers, which are connected into a three-dimensional network by hydrogen bonds to the S atoms of the anions and the O atoms of the urea molecules.

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