

# An X-Ray Investigation of Ammonium and Thallium(I) *P,P*-Dithiophospha-cyanurates

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The crystal and molecular structures for ammonium and thallium(I) *P,P*-dithiophospha-cyanurates,  $\text{NH}_4^+(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)^-$  and  $\text{Tl}^+(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)^-$ , have been determined from three-dimensional X-ray diffractometer data. The crystal structures are isotypic and the symmetry is monoclinic, space group  $P2_1/c$ . The cell dimensions are for the ammonium salt  $a = 7.204(2)$ ,  $b = 12.222(2)$ ,  $c = 9.348(1)$  Å,  $\beta = 102.15(2)^\circ$  and for the thallium salt  $a = 7.146(2)$ ,  $b = 12.208(3)$ ,  $c = 9.193(2)$  Å,  $\beta = 100.75(2)^\circ$ . The  $\text{NH}_4^+$  compound has been refined to an  $R$ -value of 0.022 for 1897 reflections and the  $\text{Tl}^+$  compound to an  $R$ -value of 0.022 for 1443 reflections. The X-ray investigations have confirmed the structural formula earlier suggested for the anion  $(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)^-$ . The anion contains a non-planar 6-membered ring  $\text{C}_2\text{N}_3\text{P}$ . Hydrogen  $\text{N}-\text{H}\cdots\text{O}$  join the anions to two endless chains related by  $\bar{1}$ .

When urea and phosphorus pentasulfide are allowed to react at temperatures about  $100^\circ\text{C}$  and the product is treated with water, large crystals are formed. The first to analyse this reaction product was Kutschig<sup>1</sup> who arrived at the tentative structural formula  $\text{NH}_4^+(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)^-$ . Subsequently, Hemmelmayr<sup>2</sup> carried out a more elaborate investigation and found the empirical formula  $\text{C}_2\text{H}_7\text{N}_4\text{PO}_2\text{S}_2$ . He also concluded that the substance was the ammonium salt of the cyclic anion  $(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)^-$ , shown in Fig. 1. Hemmelmayr has also described a number of other substances which probably also contain the *P,P*-dithiophospha-cyanurate rest. Thus he synthesized a compound which he gave the empirical formula  $\text{C}_2\text{H}_4\text{N}_3\text{PO}_2\text{S}_2 + 2\text{H}_2\text{O}$ , which may be the *P,P*-dithiophospha-cyanuric acid dihydrate. He also describes two tertiary barium salts,

one of which was given the formula  $\text{Ba}_3[(\text{C}_2\text{HN}_3\text{PO}_2\text{S}_2)\cdot\text{H}_2\text{O}]_2 + 8.5\text{H}_2\text{O}$ . Furthermore, Kutschig<sup>1</sup> prepared a primary silver salt of composition  $\text{Ag}(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)$ . Hemmelmayr's results are mentioned in reference works.<sup>3,4</sup> It is stated in Ref. 3, however, that sufficient analytical data have not been given for  $\text{C}_2\text{H}_7\text{N}_4\text{PO}_2\text{S}_2$  to ascertain the cyclic anion in the salt. As far as we are aware, no modern work concerning this anion has been carried out, and we therefore started the present investigation.

## EXPERIMENTAL

*Crystal preparation and analysis.* Crystals of  $\text{NH}_4(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)$  were prepared according to Hemmelmayr<sup>2</sup> and recrystallized several times from hot water. Elemental analyses made by Messrs. Dornis and Kolbe (Mühlheim a.d. Ruhr) gave the following results: C 11.25 (11.29); H 3.30(3.27); N 26.10(26.17); S 29.86 (29.90); P 14.53(14.48). Calculated values are given in parentheses. The empirical formula given by Hemmelmayr was thus confirmed. Suitable single crystals of the compound  $\text{Tl}(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)$  were obtained by mixing solutions of  $\text{TlNO}_3$  and  $\text{NH}_4(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)$ .

*Crystal data.* The dimensions of the monoclinic unit cells for the compounds were determined from least-squares analysis of the positions of about 30 reflections for each compound. These reflections were measured on a single crystal diffractometer with  $\text{MoK}\alpha$  radiation, the  $\theta$ -values varying between  $17$  and  $20^\circ$ . The following results were obtained:  $\text{NH}_4^+$ ;  $a = 7.204(2)$ ,  $b = 12.222(2)$ ,  $c = 9.348(1)$  Å,  $\beta = 102.15(2)^\circ$ ,  $V = 804.6$  Å<sup>3</sup>.  $\text{Tl}^+$ ;  $a = 7.146(2)$ ,  $b = 12.208(3)$ ,  $c = 9.193(2)$  Å,  $\beta = 100.75(2)^\circ$ ,  $V = 787.9$  Å<sup>3</sup>. The measured density for  $\text{NH}_4(\text{C}_2\text{H}_3\text{N}_3\text{PO}_2\text{S}_2)$ ,  $1.775$  g cm<sup>-3</sup>, was determined by flotation. The calculated densities for four formula units in the unit cell are  $1.768$  g cm<sup>-3</sup>

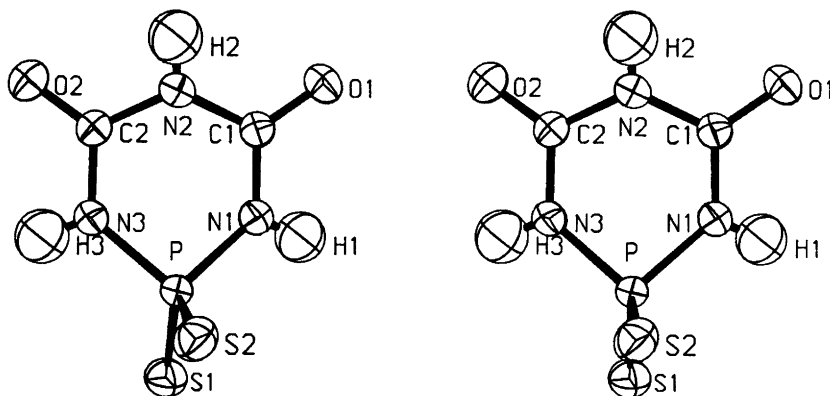


Fig. 1. Stereoscopic pair of drawings showing the anion  $(C_2H_3N_3PO_2S_2)^-$  in  $NH_4(C_2H_3N_3PO_2S_2)$ . Thermal ellipsoids are drawn to enclose 75 % probability.

for the ammonium salt and  $3.38 \text{ g cm}^{-3}$  for the thallium salt. Systematic absences of the reflections  $h0l$  with  $l=2n+1$  and  $0k0$  with  $k=2n+1$  are consistent with space group  $P2_1/c$ .

**Single crystal work.** For  $NH_4(C_2H_3N_3PO_2S_2)$  a prismatic crystal with the dimensions  $0.25 \times 0.20 \times 0.10 \text{ mm}^3$  was mounted with  $a$  along the  $\phi$  axis of the diffractometer. Intensity data were collected on a computer-controlled Enraf-Nonius CAD-4 diffractometer with  $MoK\alpha$  radiation and a graphite monochromator. The  $\omega-2\theta$  scan technique was employed with a peak scan interval  $\Delta\omega = (0.9 + 0.5 \tan \theta)^\circ$ . The scan interval was extended 25 % at both ends for the background measurements. A fast pre-scan was used to calculate the scan speed at which a minimum number of counts (3000) was obtained within a maximum measuring time (3 min.). The intensities of 2350 independent reflections were measured in the range  $3^\circ < \theta < 30^\circ$ . 453 of these were weaker than  $3\sigma(I)$ , where  $\sigma(I)$  is based on counting statistics. The remaining 1897 reflections were corrected for Lorentz, polarization and absorption effects ( $\mu_{MoK\alpha} = 8.0 \text{ cm}^{-1}$ ). Two standard reflections were measured at regular intervals.

For  $Tl(C_2H_3N_3PO_2S_2)$  a crystal with the dimensions  $0.12 \times 0.08 \times 0.06 \text{ mm}^3$  was used and the intensity data were collected and corrected in the same way as for the ammonium compound. 1804 unique reflections were measured in the range  $3^\circ < \theta < 27.5^\circ$  and 1443 of these could be considered as observed. The linear absorption coefficient was  $213 \text{ cm}^{-1}$  in this case and the transmission factors varied from 0.35 to 0.46.

#### DETERMINATION AND REFINEMENT OF THE STRUCTURES

$NH_4(C_2H_3N_3PO_2S_2)$ . The positions of the phosphorus and sulfur atoms were deduced from the three-dimensional Patterson function.

All other atoms, including the hydrogen atoms of the  $NH_4^+$  group, were found from successive difference Fourier maps. The resulting positions were refined by means of least-squares calculations using anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the hydrogens. In the final refinement a parameter was included to correct for isotropic secondary extinction. The weight factor used in the refinement was:  $w_i^{-1} = \sigma^2(|F_o|^2)/4|F_o|^2 + 0.00035|F_o|^2 + 0.32$ . The conventional  $R$ -factor was 0.022 and the weighted one 0.032 for the 1897 observed reflections. The secondary extinction parameter  $g$  was found to be  $1.4(1) \times 10^4$ , and the value of  $S$  defined by  $S = [\sum w_i(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ , where  $m$  and  $n$  are the number of observations and the number of parameters varied, respectively, was 1.0. The atomic scattering factors used for the non-hydrogen atoms were those given by Cromer and Mann<sup>5</sup> and for hydrogen those given by Stewart *et al.*<sup>6</sup>

$Tl(C_2H_3N_3PO_2S_2)$ . The positional parameters for the ammonium compound were used as starting parameters in a least-squares refinement. The weight factor used in the final refinement was  $w_i^{-1} = \sigma^2(|F_o|^2)/4|F_o|^2$ . The final agreement factors were  $R = 0.022$  and  $R_w = 0.028$  for the 1443 observed reflections. The secondary extinction parameter was found to be  $0.51(2) \times 10^4$  and  $S = 1.4$ . Final positional and thermal parameters for both compounds are given in Tables 1 and 2. Lists of observed and calculated  $|F|$ -values are available on request from the Division of Inorganic Chemistry 2. All calcu-

lations were made on the UNIVAC 1108 computer in Lund, using programs briefly described by Stålhandske.<sup>7</sup>

DISCUSSION OF THE STRUCTURE

The ammonium compound

The present structure determination of NH<sub>4</sub>(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>) has confirmed the structural formula suggested by Hemmelmayr.<sup>3</sup> The compound may thus be denoted ammonium *P,P*-dithiophospha-cyanurate. Fig. 1 shows a stereoscopic illustration of the cyclic anion and Fig. 2 gives the distances and angles within

the anion as found in the ammonium salt. Selected distances and angles in the structure with their e.s.d.'s are listed in Table 3. The phosphorus atom is tetrahedrally coordinated. The P-S distances are 1.953(1) and 1.978(1) Å, respectively, and they differ significantly. They fall as expected between the value 1.916 Å for a P-S double bond and that of 2.116 Å for a P-S single bond,<sup>8,9</sup> and they agree with those found in other dithiophosphates (see Table 4). The two P-N distances, 1.697 (2) and 1.700(2) Å agree with the P-N bond length of 1.695(4) Å (mean value) in 1,2,3,4-tetraphenyl-2,4-dithiocyclodiphosphazane [PhNP(S)Ph]<sub>2</sub>,<sup>14</sup> where the phosphorus atoms

Table 1. Final positional parameters for NH<sub>4</sub>(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>) and Tl(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>). Standard deviations are given in parentheses. The isotropic temperature factors for the hydrogen atoms are also listed.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
The ammonium compound				
N(4)	.02342(20)	.64603(12)	.91217(17)	
S(1)	.72034(5)	.67618(3)	.52247(4)	
S(2)	.95417(5)	.59720(3)	.26796(4)	
P	.73698(5)	.57509(3)	.36382(4)	
O(1)	.69908(15)	.26132(8)	.36024(13)	
O(2)	.30419(15)	.48904(9)	.06686(12)	
N(1)	.73220(17)	.44240(9)	.41737(13)	
N(2)	.53633(17)	.38417(9)	.20065(13)	
N(3)	.52683(17)	.57191(9)	.24108(14)	
C(1)	.65966(17)	.35775(10)	.33027(14)	
C(2)	.44729(18)	.48422(10)	.16422(14)	
H(1)	.8034(32)	.4261(18)	.4885(25)	2.9(4)
H(2)	.4882(33)	.3360(19)	.1506(25)	3.1(4)
H(3)	.4675(33)	.6290(20)	.2171(23)	3.2(4)
H(4)	.0479(61)	.5886(38)	.8782(48)	9.4(11)
H(5)	-.0802(49)	.6378(27)	.9595(34)	6.5(7)
H(6)	.1132(61)	.6668(33)	.9806(44)	8.3(10)
H(7)	.0041(51)	.6955(30)	.8510(40)	7.0(8)
The thallium compound				
Tl	.01162(3)	.65480(2)	.91680(3)	
S(1)	.72484(21)	.68012(11)	.52047(16)	
S(2)	.96325(19)	.59650(11)	.26276(15)	
P	.74064(19)	.57656(10)	.36010(15)	
O(1)	.69669(55)	.26383(29)	.36429(47)	
O(2)	.30799(52)	.49058(32)	.06694(43)	
N(1)	.73234(66)	.44500(35)	.41824(52)	
N(2)	.53799(67)	.38557(38)	.20194(52)	
N(3)	.53153(63)	.57349(36)	.23841(54)	
C(1)	.65874(75)	.36022(40)	.33212(63)	
C(2)	.45026(72)	.48583(42)	.16374(56)	
H(1)	.8009(90)	.4282(49)	.4984(73)	1.8(13)
H(2)	.4746(113)	.3298(66)	.1492(95)	4.0(18)
H(3)	.4870(102)	.6294(61)	.2115(78)	2.4(15)

Table 2. Anisotropic thermal parameters and their standard deviations. The temperature coefficient is expressed as  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
The ammonium compound						
N(4)	.011103(25)	.00309(8)	.00844(16)	.00064(11)	.00069(16)	-.00002(9)
S(1)	.01257(7)	.00303(2)	.00594(4)	-.00072(3)	.00215(4)	-.00121(2)
S(2)	.00908(7)	.00334(2)	.00475(4)	-.00053(3)	.00089(4)	-.00020(2)
P	.00699(6)	.00173(2)	.00437(4)	-.00036(2)	-.00045(3)	-.00008(2)
O(1)	.01124(20)	.00210(6)	.00943(14)	.00025(9)	-.00178(13)	.00049(7)
O(2)	.00891(19)	.00349(6)	.00683(12)	-.00027(9)	-.00221(11)	.00010(7)
N(1)	.00988(22)	.00219(6)	.00549(13)	-.00075(9)	-.00192(13)	.00070(7)
N(2)	.01051(22)	.00201(6)	.00544(12)	-.00009(9)	-.00107(13)	-.00039(7)
N(3)	.00834(21)	.00200(6)	.00700(14)	.00043(9)	-.00197(13)	-.00003(7)
C(1)	.00707(21)	.00223(7)	.00596(14)	-.00017(10)	.00031(14)	.00022(8)
C(2)	.00738(22)	.00247(7)	.00496(13)	-.00021(10)	.00023(13)	.00009(8)
The thallium compound						
Tl	.01052(5)	.00348(2)	.00887(4)	.00045(2)	.00097(3)	-.00039(2)
S(1)	.01134(29)	.00264(9)	.00552(17)	-.00096(12)	.00216(17)	-.00111(9)
S(2)	.00794(28)	.00342(9)	.00425(15)	-.00053(13)	.00105(16)	.00001(10)
P	.00596(24)	.00159(8)	.00387(15)	-.00032(10)	-.00041(15)	.00002(9)
O(1)	.00977(81)	.00153(23)	.00863(57)	.00018(34)	-.00142(53)	.00107(29)
O(2)	.00762(78)	.00352(28)	.00613(53)	-.00038(35)	-.00152(48)	-.00021(30)
N(1)	.00840(91)	.00215(29)	.00453(56)	-.00082(39)	-.00171(57)	.00052(32)
N(2)	.00971(96)	.00199(27)	.00497(58)	.00002(42)	-.00079(58)	.00003(32)
N(3)	.00681(90)	.00163(27)	.00614(59)	.00065(39)	-.00060(56)	.00052(33)
C(1)	.00686(95)	.00190(33)	.00621(65)	-.00024(43)	.00093(62)	-.00017(36)
C(2)	.00744(100)	.00199(32)	.00458(67)	-.00011(43)	.00082(64)	.00009(34)

are tetrahedrally coordinated. As the length of a P–N single bond is 1.77 Å,<sup>15</sup> the actual P–N bonds must have some  $\pi$  bond character. Peterson and Wagner<sup>14</sup> and Bullen, Ruther-

ford and Tucker<sup>16</sup> have discussed the influence of the non-bonded N···N distance on the P–N bond lengths in cyclic P–N compounds, and they state that a short N···N distance will at

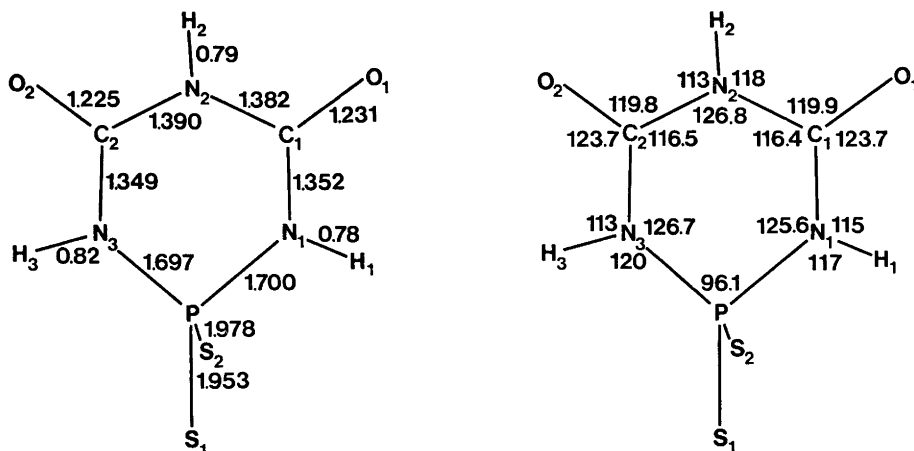


Fig. 2. Bond lengths and angles in the anion in the structure of  $\text{NH}_4(\text{C}_2\text{H}_3\text{N}_3\text{PO}_3\text{S}_2)$ .

*Table 3.* Selected distances and angles in the crystal structures of ammonium and thallium(I) *P,P*-dithiophospha-cyanurates.

Distances and angles within the (C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>)<sup>-</sup> ion

Atoms	Distances (Å) for	
	the NH <sub>4</sub> <sup>+</sup> -compound	the Tl <sup>+</sup> -compound
P-S(1)	1.953(1)	1.961(2)
P-S(2)	1.978(1)	1.980(2)
P-N(1)	1.700(2)	1.697(5)
P-N(3)	1.697(2)	1.692(5)
N(1)-H(1)	0.78(3)	0.83(7)
N(3)-H(3)	0.82(3)	0.77(8)
N(1)-C(1)	1.352(2)	1.349(7)
N(3)-C(2)	1.349(2)	1.344(7)
C(1)-O(1)	1.231(2)	1.231(7)
C(2)-O(2)	1.225(2)	1.221(7)
N(2)-H(2)	0.79(3)	0.91(9)
N(2)-C(1)	1.382(2)	1.374(8)
N(2)-C(2)	1.390(2)	1.390(7)

Atoms forming angle	Angles (°) for	
	the NH <sub>4</sub> <sup>+</sup> -compound	the Tl <sup>+</sup> -compound
S(1)-P-S(2)	115.99(2)	115.1(1)
S(1)-P-N(1)	111.82(5)	111.3(2)
S(1)-P-N(3)	109.84(5)	110.1(2)
S(2)-P-N(1)	109.31(5)	109.7(2)
S(2)-P-N(3)	112.02(5)	112.9(2)
N(1)-P-N(3)	96.13(6)	96.3(3)
P-N(1)-H(1)	117(2)	118(5)
P-N(3)-H(3)	120(2)	117(6)
P-N(1)-C(1)	125.6(1)	125.0(4)
P-N(3)-C(2)	126.7(1)	126.9(4)
C(1)-N(1)-H(1)	115(2)	116(5)
C(2)-N(3)-H(3)	113(2)	115(6)
N(1)-C(1)-O(1)	123.7(2)	123.2(6)
N(3)-C(2)-O(2)	123.7(2)	123.8(5)
O(1)-C(1)-N(2)	119.9(2)	119.9(5)
O(2)-C(2)-N(2)	119.8(2)	120.1(5)
N(1)-C(1)-N(2)	116.4(2)	116.8(5)
N(3)-C(2)-N(2)	116.5(2)	116.2(5)
C(1)-N(2)-H(2)	118(2)	118(6)
C(2)-N(2)-H(2)	113(2)	112(6)
C(1)-N(2)-C(2)	126.8(2)	126.8(5)

Distances and angles in the NH<sub>4</sub><sup>+</sup>-group in NH<sub>4</sub>(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>).

Atoms	Distance (Å)	Atoms forming angle	Angle(°)
N(4)-H(4)	0.81(5)	H(4)-N(4)-H(5)	110(4)
N(4)-H(5)	0.95(4)	H(4)-N(4)-H(6)	111(5)
N(4)-H(6)	0.85(5)	H(4)-N(4)-H(7)	113(5)
N(4)-H(7)	0.82(4)	H(5)-N(4)-H(6)	103(4)
		H(5)-N(4)-H(7)	112(4)
		H(6)-N(4)-H(7)	107(4)

Table 4. Phosphorus-sulfur distances (Å) and angles S-P-S (°) in selected dithiophosphates.

Compound	Short distance P-S	Long distance P-S	Average	Angle S-P-S	Ref.
K[S <sub>2</sub> P(OCH <sub>3</sub> ) <sub>3</sub> ]	1.960(13)	1.960(13)	1.96	118.2(9)	10
Pb[S <sub>2</sub> P(i-OC <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ] <sub>2</sub>	1.93 1.95	1.99 2.03	1.98		11
Pb[S <sub>2</sub> P(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	1.968(7) 1.969(7)	1.991(9) 1.995(8)	1.98	116.2(4) 115.4(3)	12
Zn[S <sub>2</sub> P(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	1.973(11) 1.992(7)	1.987(9) 2.001(5)	1.99	109.7(4) 108.0(3)	13
NH <sub>4</sub> (C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> PO <sub>2</sub> S <sub>2</sub> )	1.953(1)	1.987(1)	1.97	115.99(2)	present work
Tl(C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> PO <sub>2</sub> S <sub>2</sub> )	1.961(2)	1.980(2)	1.97	115.1(1)	present work

least to some degree lengthen the P-N distance. However, the effect seems to be small, judging from the P-N distances mentioned above and the non-bonded N...N interactions in C<sub>2</sub>H<sub>7</sub>N<sub>4</sub>PO<sub>2</sub>S<sub>2</sub> and in [PhNP(S)Ph]<sub>2</sub> which are 2.53 and 2.22 Å, respectively.

The anion (C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>)<sup>-</sup> may be regarded as a substituted biuret molecule, where N-H bonds of the terminal nitrogen atoms have been replaced by N-P bonds (*cf.* Fig. 1) thus forming the cyclic anion.

The anion (C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>)<sup>-</sup> is not planar (Fig. 1) and the same applies to its biuret part. The N, C, and O atoms of each urea part lie in a plane to within 0.003 Å. The dihedral angle between these parts is 163.8(3)°, whereas the corresponding angle in perdeuterated biuret hydrate is 173.7°. The 6-membered ring C<sub>2</sub>N<sub>3</sub>P has a shallow boat form (Fig. 1).

*Intermolecular distances and hydrogen bonding.* There are two short intermolecular contacts between the anions of the present crystal structure. One, which occurs between S(1) (*x, y, z*) and C(1) (*-x, -y, -z*) is found to be 3.340(1) Å. Using the van der Waals radii 1.70 Å for C (*cf.* Pauling<sup>8</sup>) and 1.72 Å for sulfur (Lee and Goodacre<sup>9</sup>) the sum of the radii will be 3.42 Å. The other short contact of 3.338(3) Å occurs between C(2) (*x, y, z*) and C(2) (*-x, -y, -z*). All other intermolecular contacts are equal to or longer than the corresponding van der Waals radii.

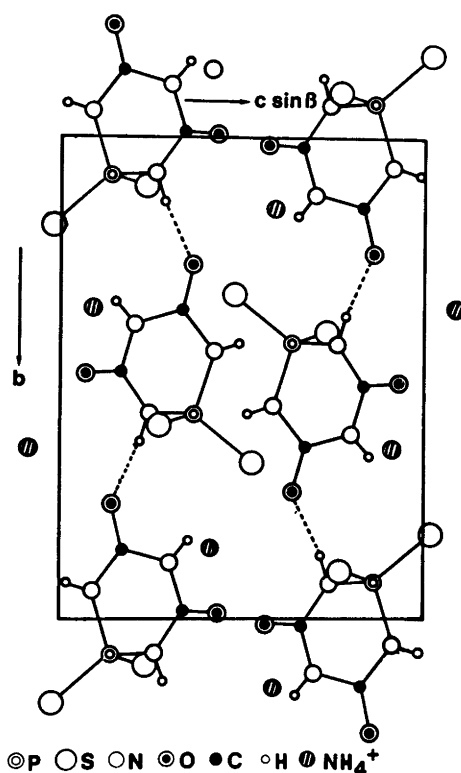


Fig. 3. Projection of the crystal structure of NH<sub>4</sub>(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>) along the *a* axis. Supposed hydrogen bonds N(3)-H(3)...O(1) are indicated by dashed lines.

Table 5. Distances less than 3.60 Å from R<sup>+</sup> to other non-hydrogen atoms. R<sup>+</sup> denotes Tl<sup>+</sup> and NH<sub>4</sub><sup>+</sup> and *x*, *y*, *z* refer to the coordinates given in Table 1.

Distance from R <sup>+</sup> ( <i>x,y,z</i> ) to	Distances (Å) for Tl <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>
S(1) ( <i>x</i> -1,1.5- <i>y</i> ,0.5+ <i>z</i> )	3.146(2)	3.391(2)
S(2) ( <i>x</i> -1, <i>y</i> ,1+ <i>z</i> )	3.339(1)	3.517(2)
S'(2) ( <i>x</i> -1,1.5- <i>y</i> ,0.5+ <i>z</i> )	3.341(2)	3.411(2)
S''(2) (1- <i>x</i> ,1- <i>y</i> ,1- <i>z</i> )	3.504(2)	3.437(2)
Average: R <sup>+</sup> -S(2)	3.40	3.46
O(1) (1- <i>x</i> ,0.5+ <i>y</i> ,1.5- <i>z</i> )	2.933(4)	2.953(2)
O(2) (- <i>x</i> ,1- <i>y</i> ,1- <i>z</i> )	2.918(4)	2.920(2)
O'(2) ( <i>x,y</i> ,1+ <i>z</i> )	3.053(4)	2.938(2)
N(2) (1- <i>x</i> ,1- <i>y</i> ,1- <i>z</i> )		3.566(2)
C(1) (1- <i>x</i> ,1- <i>y</i> ,1- <i>z</i> )	3.582(7)	3.540(2)

As the positions of the hydrogen atoms in the ammonium group are determined with low accuracy and a neutron diffraction study is in progress, the discussion of the hydrogen bonding system involving the ammonium group will be made in a forthcoming paper. The distance of 2.874(2) Å may correspond to a N-H...O hydrogen bond between O(1) (*x,y,z*) and N(3) (-*x*,½+*y*,½-*z*). By means of this postulated hydrogen bond the anions of the crystal structure are joined to two separate but structurally equivalent endless chains (Fig. 3). The two chains may in turn be linked by hydrogen bonds *via* the ammonium ions.

*Coordination of the ammonium ions.* Distances less than 3.60 Å between amino nitrogen and other atoms of the crystal structure are listed in Table 5. The seven shortest distances occur to sulfur and oxygen atoms. Using the radii values 1.40, 1.84 and 1.48 Å for O<sup>2-</sup>, S<sup>2-</sup> and

NH<sub>4</sub><sup>+</sup>, respectively, as given in Ref. 8, the expected NH<sub>4</sub>-S and NH<sub>4</sub>-O distances will be 3.32 and 2.88 Å, respectively. The four NH<sub>4</sub>-S distances actually found range between 3.39 and 3.52 Å, and the three NH<sub>4</sub>-O distances range between 2.92 and 2.95 Å. The resulting seven-fold coordination around N (NH<sub>4</sub><sup>+</sup>) is quite irregular, but may be described as an one-capped trigonal prism (*cf.* Fig. 4). The basal planes of the trigonal prism (O2,S1, S2 and S2'',S2',O2') form a dihedral angle of 3°. It may also be mentioned that one of the quadrangular faces of the polyhedron is planar by symmetry and the other is planar within 0.3 Å.

#### The thallium compound

Table 3 gives corresponding distances and angles in the crystal structures of ammonium

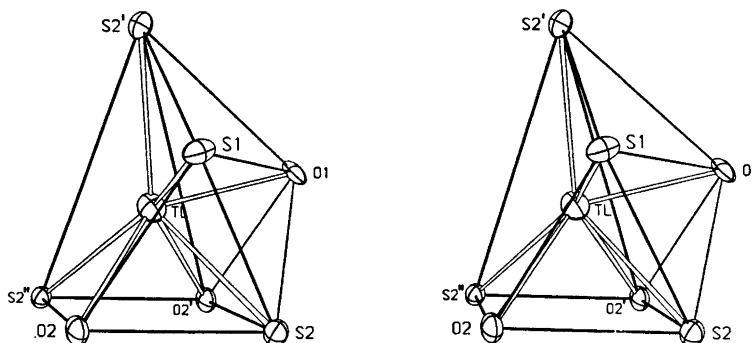


Fig. 4. Stereoscopic illustration of the seven-fold coordination of thallium (I) in Tl(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>). For notations and distances, see Table 5. The same illustration applies to the isotopic compound NH<sub>4</sub>(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>).

and thallium(I) *P,P*-dithiophosphacyanurates. Considering at first only the atoms of the 6-membered ring,  $C_2N_3P$ , it is seen that no significant differences occur between the distances and angles. Considering the Tl-S and Tl-O distances less than 3.60 Å, Tl is coordinated to four sulfur atoms and to three oxygen atoms (Table 5). The Tl-S(1) distance is 0.25 Å shorter than the average of the three Tl-S(2) distances. The corresponding difference for the ammonium compound is 0.07 Å. As the ionic radii of  $Tl^+$  and  $NH_4^+$  do not differ very much (see Ref. 8) it may be concluded that  $Tl^+$  is relatively more firmly bonded to the S(1) atom than  $NH_4^+$ . This situation is also reflected in the observed P-S(1) distances, 1.961(2) Å for the thallium compound and 1.953(1) Å for the ammonium compound. The seven-fold coordination of thallium (Fig. 4) is almost identical to that found for the ammonium compound. However, a fifth sulfur atom S(1) ( $x-1, y, z$ ) is situated at a distance of 3.84 Å from the  $Tl^+$  ion and a two-capped trigonal prism results if this atom is included in the coordination polyhedron. These seven and eight coordinations are in good agreement with those found for other thallium(I) compounds. Thus Jennische and Hesse<sup>18</sup> in their study of thallium(I) dimethyldithiocarbamate found that  $Tl^+$  was coordinated to seven sulfur atoms at distances of 2.99–3.74 Å, the coordination polyhedron being a one-capped trigonal prism, less distorted than that given in Fig. 4. As seen from Table 5, four Tl-S distances in the present compound fall in the range 3.146(2) to 3.504(2) Å. These distances may be regarded as mainly ionic, as the sum of the ionic radii<sup>8</sup> is 3.28 Å. The fifth Tl-S distance of 3.84 Å indicates only a weak interaction. A summary of selected Tl(I)-S distances has recently been given by Esperås and Husebye.<sup>19</sup> The distances observed for the present compound fall in the range reported by them. The three Tl-O distances (Table 5) vary between 2.918(4) and 3.053(4) Å, and these interactions are also mainly ionic as the sum of the ionic radii<sup>8</sup> is 2.80 Å.

### Conclusion

Two isotopic salts of the hypothetical *P,P*-dithiophosphacyanuric acid have been investigated, *viz.* the ammonium and the thallium(I)

salts. No significant differences occur for the  $(C_2H_3N_3PO_3S_2)^-$  anions in the two structures. The six-membered ring skeleton  $C_2N_3P$  deviates from planarity and has a shallow boat form. The phosphorus atom is tetrahedrally coordinated. In the crystal structures the anions  $(C_2H_3N_3PO_3S_2)^-$  are joined by N-H...O hydrogen bonds to two endless chains related by  $\bar{1}$ . The chains may in turn be joined by hydrogen bonds *via* the ammonium ions to a three-dimensional network.

*Acknowledgements.* This work received financial support from the Swedish Natural Science Research Council.

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Received February 20, 1975.