Crystal structure of pyridinium salt of 2,4-dithioxo-2,4-dimercapto-1,3-diaza-2 λ^5 ,4 λ^5 -diphosphetidine, C₁₆H₃₀N₄P₂S₄Si₂

J. Marek and J. Příhoda

Masaryk University, Department of Inorganic Chemistry, Kotlářská 2, 611 37 Brno, Czech Republic

Received November 5, 1996, CSD-No. 402689

C₁₆H₃₀N₄P₂S₄Si₂, monoclinic,
*P*12₁/*n*1 (No. 14), *a* = 14.497(3) Å,
b = 10.321(2) Å, *c* = 17.698(7) Å,
 β = 91.34(2)°, *V* = 2647.3 Å³, *Z* = 4,
R(*F*) = 0.034, *R*_w(*F*²) = 0.094.

Source of material: See ref 1. Crystals were obtained from acetonitrile. Melting point is not available because of the thermal decomposition (see ref. 2).

The crystal has four salt molecules in unit cell. The asymmetric unit has two half of salt molecules and the molecules are centrosymmetric dimers close to symmetry *D*_{2h}. Consequently the four-membered phosphazane rings are planar. The Si atoms Si1 and Si11 deviate by 0.18 Å and 0.32 Å from planes through P1 and N1 (resp. P11 and N11) atoms and their symmetrical equivalents. The deviations of equivalent S atoms from the same planes are practically identical, the values of the deviation lie in the interval 1.61–1.68 Å. The average bond lengths are P–N = 1.697 Å and P–S = 1.972 Å. The first value is very close to the values in similar compounds (see refs. 3–5) and indicate some π -bond character of N–P bond. The second bond length is significantly longer than double S–P bond in compounds in refs. 3–5 and indicates delocalisation of the double bond between both sulfur atoms.

Table 1. Parameters used for the X-ray data collection

Crystal:	yellow prism, size 0.50 x 0.50 x 0.60 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.82 cm ⁻¹
Diffractometer:	KUMA KM-4 κ -axis
Scan mode:	$\omega/2\theta$
<i>T</i> _{measurement} :	293 K
2 θ _{max} :	46°
<i>N</i> (<i>hkl</i>) _{unique} :	3384
Criterion for <i>I</i> _o :	<i>I</i> _o > 2 σ (<i>I</i> _o)
<i>N</i> (<i>param</i>) _{refined} :	373
Programs:	SHELXS-86, SHELXL-93, ORTEP

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2D)	4e	0.637(3)	0.505(4)	0.670(3)	0.06(1)
H(1A)	4e	0.968(3)	0.381(4)	0.961(2)	0.05(1)
H(1B)	4e	0.871(3)	0.321(4)	0.956(2)	0.04(1)
H(1C)	4e	0.903(3)	0.439(4)	0.996(2)	0.04(1)
H(2A)	4e	0.844(3)	0.309(5)	1.152(3)	0.06(1)
H(2B)	4e	0.807(4)	0.197(5)	1.108(3)	0.08(2)
H(2C)	4e	0.871(3)	0.180(5)	1.165(3)	0.06(2)
H(3A)	4e	1.098(3)	0.332(4)	1.083(3)	0.05(2)
H(3B)	4e	1.038(3)	0.400(4)	1.133(2)	0.04(1)
H(3C)	4e	1.065(4)	0.264(6)	1.150(3)	0.10(2)
H(5)	4e	0.753(3)	0.394(4)	0.612(2)	0.02(2)
H(6)	4e	0.867(3)	0.302(4)	0.653(3)	0.05(1)
H(8)	4e	0.798(3)	0.464(4)	0.841(3)	0.04(1)
H(7)	4e	0.898(2)	0.338(3)	0.772(2)	0.02(1)
H(9)	4e	0.676(3)	0.536(4)	0.785(3)	0.05(1)
H(12D)	4e	0.849(3)	-0.011(3)	0.344(2)	0.03(1)
H(11A)	4e	0.946(3)	0.384(5)	0.519(3)	0.08(2)
H(11B)	4e	0.950(3)	0.438(5)	0.436(3)	0.06(1)
H(11C)	4e	0.881(3)	0.328(5)	0.443(3)	0.08(2)
H(12A)	4e	1.052(4)	0.311(7)	0.301(3)	0.11(2)
H(12B)	4e	0.975(5)	0.228(8)	0.309(5)	0.15(4)
H(12C)	4e	1.068(6)	0.17(1)	0.303(5)	0.19(4)
H(13A)	4e	1.133(4)	0.316(6)	0.524(4)	0.10(3)
H(13B)	4e	1.161(4)	0.406(5)	0.452(3)	0.09(2)
H(13C)	4e	1.191(4)	0.260(5)	0.453(3)	0.08(2)
H(14)	4e	0.625(2)	0.173(4)	0.340(2)	0.02(1)
H(15)	4e	0.590(3)	0.128(5)	0.211(3)	0.08(2)
H(16)	4e	0.699(2)	-0.009(3)	0.166(2)	0.01(1)
H(17)	4e	0.831(3)	-0.068(4)	0.229(3)	0.05(1)
H(19)	4e	0.751(3)	0.109(3)	0.401(2)	0.03(1)

Table 3. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
S(1)	4e	1.17390(6)	0.11095(9)	0.96097(6)	0.0198(5)	0.0355(5)	0.0320(6)	-0.0089(4)	-0.0038(4)	0.0024(4)
S(2)	4e	0.99353(6)	0.09342(9)	0.84718(5)	0.0239(5)	0.0323(5)	0.0270(7)	-0.0049(4)	-0.0051(4)	0.0054(4)
Si(1)	4e	0.95329(6)	0.25151(9)	1.06003(6)	0.0259(5)	0.0181(5)	0.0321(7)	-0.0005(4)	-0.0004(4)	0.0013(4)
P(1)	4e	1.04505(6)	0.05432(8)	0.94957(5)	0.0182(5)	0.0187(5)	0.0236(6)	-0.0034(4)	-0.0015(4)	0.0014(4)
N(1)	4e	0.9771(2)	0.1001(2)	1.0217(2)	0.023(2)	0.020(1)	0.025(2)	-0.002(1)	0.002(1)	0.004(1)
S(11)	4e	0.82103(6)	0.07838(9)	0.54595(6)	0.0208(5)	0.0396(5)	0.0347(7)	0.0065(4)	-0.0023(4)	0.0004(5)
S(12)	4e	1.01580(7)	0.1304(1)	0.64116(6)	0.0321(5)	0.0442(6)	0.0348(7)	0.0148(5)	-0.0132(4)	-0.0156(5)
Si(11)	4e	1.03529(7)	0.24894(9)	0.43196(7)	0.0333(6)	0.0236(5)	0.0490(8)	0.0039(4)	0.0051(5)	0.0078(5)
P(11)	4e	0.95518(6)	0.05553(8)	0.54974(5)	0.0209(5)	0.0223(5)	0.0245(6)	0.0051(4)	-0.0023(4)	-0.0019(4)
N(11)	4e	1.0071(2)	0.0962(3)	0.4687(2)	0.025(2)	0.022(2)	0.033(2)	0.006(1)	0.001(1)	0.000(1)
C(1)	4e	0.9191(4)	0.3593(4)	0.9818(3)	0.039(3)	0.024(2)	0.053(3)	0.000(2)	-0.007(2)	0.007(2)
C(2)	4e	0.8582(3)	0.2316(5)	1.1263(3)	0.042(3)	0.029(2)	0.052(3)	0.001(2)	0.010(2)	-0.004(2)
C(3)	4e	1.0554(3)	0.3154(4)	1.1120(3)	0.041(3)	0.026(2)	0.047(3)	-0.003(2)	-0.005(2)	-0.002(2)
N(2)	4e	0.7011(2)	0.4728(3)	0.6858(2)	0.025(2)	0.037(2)	0.042(3)	0.008(2)	-0.009(2)	0.002(2)
C(5)	4e	0.7586(3)	0.4002(4)	0.6488(4)	0.042(3)	0.045(3)	0.032(4)	-0.006(2)	-0.009(2)	-0.009(2)
C(6)	4e	0.8351(3)	0.3503(4)	0.6824(3)	0.041(3)	0.039(2)	0.038(3)	0.010(2)	0.002(2)	-0.009(2)
C(7)	4e	0.8509(3)	0.3760(4)	0.7562(3)	0.027(2)	0.045(2)	0.052(4)	0.012(2)	-0.007(2)	0.009(2)
C(8)	4e	0.7914(3)	0.4517(4)	0.7949(3)	0.033(3)	0.047(3)	0.036(3)	0.001(2)	-0.007(2)	-0.007(2)
C(9)	4e	0.7150(3)	0.4992(4)	0.7578(3)	0.034(2)	0.038(2)	0.042(4)	0.007(2)	0.007(2)	-0.006(2)
C(11)	4e	0.9416(3)	0.3597(4)	0.4580(3)	0.031(2)	0.027(2)	0.082(4)	0.002(2)	-0.008(2)	0.005(2)
C(12)	4e	1.0406(7)	0.2348(6)	0.3280(4)	0.156(8)	0.047(3)	0.052(4)	0.005(4)	0.025(4)	0.019(3)
C(13)	4e	1.1467(4)	0.3045(5)	0.4730(5)	0.032(3)	0.039(3)	0.149(8)	-0.007(2)	0.001(4)	0.013(4)
C(15)	4e	0.6440(3)	0.0908(4)	0.2450(3)	0.035(2)	0.038(2)	0.052(3)	-0.004(2)	-0.008(2)	0.008(2)
N(12)	4e	0.7970(2)	0.0121(3)	0.3190(2)	0.023(2)	0.027(2)	0.062(3)	0.001(2)	-0.014(2)	0.008(2)
C(17)	4e	0.7831(3)	-0.0265(4)	0.2486(3)	0.028(2)	0.027(2)	0.066(4)	0.000(2)	0.013(2)	-0.002(2)
C(19)	4e	0.7392(3)	0.0895(4)	0.3542(3)	0.049(3)	0.036(2)	0.030(3)	-0.004(2)	-0.008(2)	-0.002(2)
C(16)	4e	0.7059(3)	0.0125(4)	0.2102(3)	0.047(3)	0.042(3)	0.029(3)	-0.007(2)	0.001(2)	-0.007(2)
C(14)	4e	0.6613(3)	0.1299(4)	0.3177(3)	0.036(2)	0.031(2)	0.054(4)	0.011(2)	0.010(2)	-0.006(2)

Acknowledgment. This work was supported by the Grant Agency of the Czech Republic, grant No. 203/95/1190.

References

- Prřhoda, J.; Grossmann, G.; Ohms, G.; Meisel, M.: Synthese, Eigenschaften und NMR-spektroskopische Untersuchungen an 2,4-Dithioxo-2,4-dimercapto-1,3-diaza-2 λ^5 ,4 λ^5 -diphosphetidenen. *Z. Anorg. Allg. Chem.* **549** (1987) 59-66.
- Prřhoda, J.; Meindl, J.: Thermal Decomposition of the Pyridinium Salt of 1,3-bis(trimethylsilyl)-2,4-dimercapto-2,4-dithioxo-1,3-diaza-2 λ^5 ,4 λ^5 -diphosphetidine. *J. Thermal. Anal.* **36** (1990) 2505-2510.
- Bullen, G. J.; Rutherford, J. S.; Tucker, P. A.: The Crystal and Molecular Structure of *trans*-1,3-Diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazene. *Acta Crystallogr. B* **29** (1973) 1439-1445.
- Bullen, G. J.; Tucker, P. A.: The Crystal and Molecular Structure of *cis*-1,3-Diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazene. *Acta Crystallogr. B* **29** (1973) 2878-2884.
- Cameron, T. S.; Prout, C. K.; Howlett, K. D.: The Crystal Structure of *trans*-1,3-Dimethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazene, [PhP(S)NMe]₂. *Acta Crystallogr. B* **31** (1975) 2333-2335.
- Sheldrick, G. M.: SHELXS-86, a program for crystal structure solution. University of Göttingen, Germany 1986.
- Sheldrick, G. M.: SHELXL-93, a program for refining of crystal structures. University of Göttingen, Germany 1993.
- Johnson, C. K.: ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA 1965.