oxygen atom is hydrogen bonded to two amino groups in an adjacent complex, and the other carboxyl oxygen is hydrogen bonded to an amino group in a different complex as well as to the water molecule. This is the only contact made by the water molecule which can be unequivocably assigned as a hydrogen bond.

The perchlorate oxygens have characteristically high thermal parameters but are not disordered. The bond lengths and angles are normal, and the hydrogen bonding involving the perchlorate groups is very weak.

Registry No. Λ-*N,S*-[Co(en)$_2$(*R*)cysS]ClO$_4$, 66417-03-6; Λ-*N,S*-[Co(en)$_2$(*R*)cysS](ClO$_4$)$_2$, 66417-02-5; Δ-*N,S*-[Co(en)$_2$(*R*)cysS](ClO$_4$)$_2$, 66417-01-4; Δ-*N,S*-[Co(en)$_2$(*R*)cysS]ClO$_4$·H$_2$O, 66417-00-3; Λ-*N,S*-[Co(en)$_2$(*R*)cysSH](ClO$_4$)$_3$, 66513-17-5; Λ-*N,S*-[Co(en)$_2$(*S*)penS]S$_2$O$_6$, 66416-98-6; Δ-*N,S*-[Co(en)$_2$(*S*)penS](ClO$_4$)$_2$, 66416-97-5; Λ-*N,S*-[Co(en)$_2$(*R*)cysS]Cl$_2$, 66416-96-4; Δ-*N,S*-[Co(en)$_2$(*R*)cysS]Cl$_2$, 66416-95-3; Λ-*N,S*-[Co(en)$_2$(*S*)penS]Cl$_2$, 66416-94-2; Δ-*N,S*-[Co(en)$_2$(*S*)penS]Cl$_2$, 66416-93-1; Co(en)$_2$(NH$_2$(CH$_2$)$_2$S)$^{2+}$, 42901-32-6; Co(en)$_2$SCH$_2$OCO$^+$, 42901-31-5.

Supplementary Material Available: Listings of structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Sydney. (b) Australian National University.
(2) Abbreviations used: cysS = cysteine deprotonated at sulfur; similarly, penS = penicillamine. To avoid confusion, no formal distinction is made between the ions with or without the carboxylate proton since this should be evident from the bonding mode, indicated as a prefix (e.g., N,S or N,O), and the formal charge carried by the ion.
(3) (a) V. M. Kothari and D. H. Busch, *Inorg. Chem.*, **8**, 2276 (1969); (b) C. P. Sloan and J. H. Krueger, *ibid.*, **14**, 1481 (1975).
(4) "International Tables for X-Ray Crystallography", Vol. 1, Kynoch Press, Birmingham, England, 1952, p 105.
(5) Reference 4, Vol. 4, 1974, p 8.
(6) L. V. Azaroff, *Acta Crystallogr.*, **8**, 701 (1955).
(7) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(8) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(9) Reference 4, Vol. 4, 1974, pp 99 and 148.
(10) (*R,R*)-Cystine ≡ (NH$_2$CH(CO$_2$H)CH$_2$S)$_2$, the oxidized form of (*R*)-cysteine ≡ L-(−)-cystine.
(11) C. J. Weschler and E. Deutsch, *Inorg. Chem.*, **12**, 2682 (1973), and references therein.
(12) L. E. Asher and E. Deutsch, *Inorg. Chem.*, **12**, 1774 (1973).
(13) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973).
(14) R. H. Lane and L. E. Bennett, *J. Am. Chem. Soc.*, **92**, 1089 (1970).
(15) W. G. Jackson, A. M. Sargeson, and P. A. Tucker, *J. Chem. Soc., Chem. Commun.*, 199 (1977).
(16) Based on simple organic derivatives.
(17) Since this work was completed, Krueger et al.[3] prepared [Co(en)$_2$(*R*)cysS]ClO$_4$ by this route. The diastereoisomerism was ignored, and although the yield was not stated, our results indicate that, under their conditions, the Λ isomer was obtained in ≤30% yield.
(18) Reference 3a states that both the –CH– and –CH$_2$ protons of the cysteine moiety in Co(en)$_2$(*R*)cysS$^+$ exchange in 0.1 M NaOD, although no direct indication of time scale is given. Decomposition was evident, and it seems likely that the ^{1}H NMR changes observed were at least partly attributable to mutarotation.
(19) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 5133 (1967).
(20) D. A. Buckingham and A. M. Sargeson, *Top. Stereochem.*, **6**, 252 (1971).
(21) G. J. Gainsford, W. G. Jackson, and A. M. Sargeson, *J. Am. Chem. Soc.*, **99**, 2383 (1977), and unpublished work.
(22) H. C. Freeman, *Adv. Protein Chem.*, **22**, 257 (1967).
(23) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843, and the Laboratoire de Chimie Minerale Moleculaire, Equipe de Recherche Associee au CNRS, Parc Valrose, 06034, Nice Cedex, France

Structure, Bonding, and Chemistry of *closo*-Tetraphosphorus Hexakis(methylimide), P$_4$(NCH$_3$)$_6$, and Its Derivatives. 2. Polymorphs of the Monothio Derivative

F. ALBERT COTTON,*[1a] JEAN G. RIESS,*[1b] CATHERINE E. RICE,[1a] and B. RAY STULTS[1a]

Received March 21, 1978

The title compound can be obtained in two crystalline polymorphs. By sublimation one obtains an orthorhombic form: space group *Pbc*2$_1$, a = 12.658 (4) Å, b = 14.940 (3) Å, c = 16.448 (4) Å, V = 3110 (1) Å^3, Z = 8, d_x = 1.41 g cm^{-3}. By recrystallization one obtains a monoclinic form: space group $P2_1/n$, a = 14.182 (3) Å, b = 13.681 (3) Å, c = 7.934 (2) Å, β = 101.09 (2)°, V = 1510 (1) Å^3, Z = 4, d_x = 1.45 g cm^{-3}. In both cases the X-ray data are of only mediocre quality; the molecular dimensions are therefore determined with relatively low accuracy but are consistent over the three crystallographically independent molecules that comprise the two crystal forms. The molecule has virtual C_{3v} symmetry. Only two of the three types of P–N distances have significantly different lengths (Å): SP–NP, 1.63 (2); SPN–P, 1.73 (2); P–NP, 1.70 (1). The P–S bond length is 1.92 (1) Å. Other dimensions are normal.

Introduction

A program of study of the structural and spectroscopic properties of the closo *N*-methylphosphoramide P$_4$(NMe)$_6$ and its derivatives, with the objective of elucidating the bonding in these systems, has been under way for several years.[2-6] Structures of many of the sulfur and oxygen derivatives have been determined and a variety of spectroscopic studies made. This is the second of a series of detailed reports on these studies.

In the case of SP$_4$(NMe)$_6$, we first determined the structure using a crystal grown by sublimation. This was found to have a large orthorhombic unit cell with two molecules in the asymmetric unit, and, unfortunately, the amount of data which could be collected was disappointingly small, namely, only 1466 observed reflections for 246 parameters (for a ratio of 6.0). Moreover, there were sizable variations in the values obtained for what should have been equivalent bond lengths and angles. Therefore, an effort was made to obtain a crystal of better quality by slow crystallization from hexane solution. It was found that the crystals so obtained were of a different polymorph, belonging to a monoclinic space group. Although the data to parameter ratio (6.2) is only marginally better than for the orthorhombic form, the structural features are somewhat more precisely defined. In any event, the second structure affords independent confirmation of the pattern of variation of P–N bond lengths, a feature of key importance in attempting to understand the molecular electronic structure. We report here both crystal structure determinations and present and discuss the best values of molecular dimensions thus obtained.

Experimental Section

The preparation of SP$_4$(NCH$_3$)$_6$ has been described previously.[6] The material was sublimed in an evacuated (10^{-3} mmHg), sealed tube placed horizontally in a temperature gradient (25–65 °C) for ca. 4

0020-1669/78/1317-3521$01.00/0 © 1978 American Chemical Society

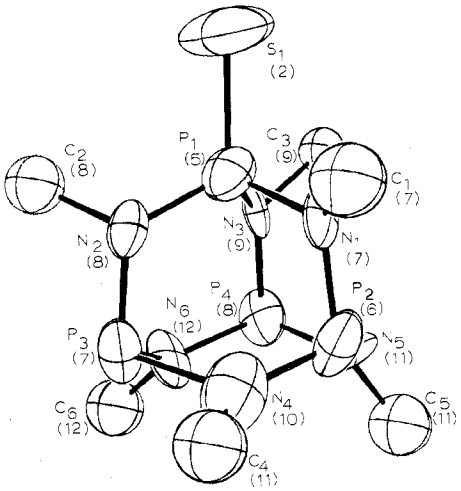


Figure 1. Molecular structure of $SP_4(NMe)_6$ showing the atom numbering scheme. Atoms of the first of the two crystallographically independent molecules of the orthorhombic form and the atoms of the unique molecule in the monoclinic form are given the designations S_1, P_1, N_1, etc. The numbers of corresponding atoms in the second molecule of the orthorhombic form are shown directly beneath these, in parentheses.

days. Crystal 1 was chosen for X-ray study. A small quantity of orthorhombic $SP_4(NCH_3)_6$ was recrystallized from dry hexane under Ar at −15 °C. A crystal of the recrystallized material (monoclinic phase) of dimensions 0.4 × 0.4 × 0.15 mm was used (crystal 2). Both crystals were sealed in thin-walled glass capillaries for data collection to prevent slow decomposition in the air while in the X-ray beam.

Film and diffractometer measurements for the crystals were compatible with the space groups $Pbc2_1$ (a nonstandard setting of $Pca2_1$, No. 29) for crystal 1 and $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14) for crystal 2.

Unit cell parameters and intensities were measured at 21 ± 2 °C on a Syntex $P\bar{1}$ automated diffractometer using graphite-monochromated Mo Kα radiation. The automatic centering and indexing procedures followed have been detailed elsewhere.[7] Cell parameters and their estimated standard deviations, shown in Table I, were calculated by the least-squares refinement of the observed 2θ values for 15 reflections for each crystal, $20 < 2\theta < 30°$.

The intensities of all unique reflections were collected with $0 < 2\theta \leq 55°$ for crystal 1 and $0 < 2\theta \leq 45°$ for crystal 2, yielding 3730 and 1985 unique data, respectively. The θ–2θ scan technique was used with variable scan rates from 3.0 to 24.0°/min and with scan ranges from 2θ(Mo Kα_1) − 0.8° to 2θ(Mo Kα_2) + 0.8° for crystal 1 and from 2θ(Mo Kα_1) − 1.2° to 2θ(Mo Kα_2) + 1.2° for crystal 2 (reflections for crystal 2 had fairly broad peak profiles, typical ω scans having a full width at half-maximum of 0.35°). The intensities of standard reflections monitored after every few hours of data collection showed no significant variations. The data were corrected for Lorentz and polarization effects,[7] but absorption corrections were omitted since even for crystal 2 the maximum and minimum transmission factors are calculated to be 0.91 and 0.86, respectively. Only those reflections with $I \geq 3\sigma(I)$ (1466 for crystal 1, 1761 for crystal 2) were considered observed and were included in subsequent refinements.

Table I. Crystallographic Data for $SP_4(NCH_3)_6$

parameter	orthorhombic phase	monoclinic phase
a, Å	12.658 (4)	14.182 (3)
b, Å	14.940 (3)	13.681 (3)
c, Å	16.448 (4)	7.934 (2)
β, deg	90	101.09 (2)
V, Å^3	3110 (1)	1510 (1)
Z	8	4
d_x, g/cm^3 [a]	1.41	1.45
n[b]	1466	761
R_1	0.096	0.073
R_2	0.098	0.092

[a] Calculated from unit cell dimensions and Z. [b] Number of reflections with $I \geq 3\sigma(I)$ used in refinement.

The structures of both the orthorhombic and monoclinic phases of $SP_4(NCH_3)_6$ were solved using direct methods.[8] For the orthorhombic form, atomic coordinates for the eight phosphorus atoms (two molecules in the asymmetric unit) were derived from an E map calculated from the phase set having the second highest figure of merit produced by the program MULTAN operating on an input of the 350 reflections with the highest E values. A series of difference Fourier maps, each following refinement of the positions of the atoms located to that point, were used to locate the remaining nonhydrogen atoms. No attempt has been made to distinguish the correct polarity (enantiomorph) of this crystal. It was clear from the behavior of the refinement based on the half-set of data initially collected and used to solve the structure that no worthwhile improvement (and probably no improvement at all significant in a statistical sense) could be obtained by adding the other half of the data. At the risk of belaboring the obvious, the half-set of data was collected because the systematic absences are consistent also with the space group $Pbcm$ and it was hoped that this would be the correct one so that the "half-set" would be a full set.

For monoclinic $SP_4(NCH_3)_6$, all 17 nonhydrogen atoms (one molecule in the asymmetric unit) were located from the E map calculated from the phase set having the highest figure of merit, using the 290 reflections with E values greater than 1.40. Both structures were refined to convergence by full-matrix least-squares methods, using isotropic thermal parameters for the carbon atoms and anisotropic thermal parameters for all other atoms. The quantity minimized in the refinements was $\sum w(F_o - F_c)^2$, where $w = 4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for ρ in the calculation of σ. The atomic scattering factors used were those of Cromer and Waber[9] for neutral atoms, and anomalous dispersion terms[10] were included for all atoms. The final refinement results are shown in Table I, where $R_1 = \sum||F_o| - |F_c||/|F_o|$ and $R_2 = [\sum w(||F_o| - |F_c||)^2/\sum w|F_o|^2]^{1/2}$. For both structures, the final difference Fourier maps were free of any significant residual electron density. Values of observed and calculated structure factors are available as supplementary material.

Results and Discussion

The positional and thermal parameters are listed in Tables II and III for the orthorhombic and monoclinic polymorphs,

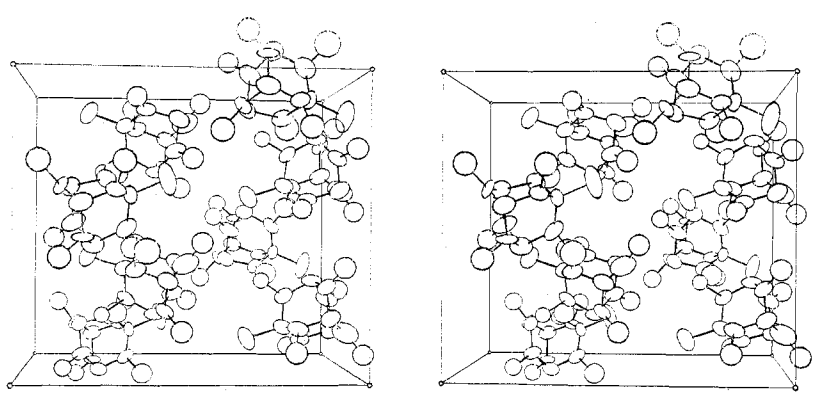


Figure 2. ORTEP stereoview of the unit cell of the orthorhombic form, showing the molecular packing.

Table II. Positional and Thermal Parameters[a,b] for Orthorhombic $SP_4(NMe)_6$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.4904 (8)	0.1049 (6)	0.3050 (0)	0.035 (1)	0.0113 (5)	0.0059 (3)	−0.006 (1)	0.003 (1)	0.0065 (7)
S(2)	0.0260 (7)	0.3514 (7)	0.0712 (4)	0.026 (1)	0.0199 (8)	0.0047 (3)	0.009 (1)	0.001 (1)	−0.0075 (8)
P(1)	0.4971 (4)	0.1468 (4)	0.1914 (3)	0.0092 (4)	0.0055 (3)	0.0064 (3)	−0.0005 (6)	0.0008 (7)	0.0024 (5)
P(2)	0.6388 (4)	0.1860 (4)	0.0586 (4)	0.0080 (4)	0.0064 (3)	0.0076 (3)	−0.0050 (6)	0.0062 (6)	−0.0034 (6)
P(3)	0.4146 (4)	0.1281 (4)	0.0261 (4)	0.0074 (4)	0.0071 (3)	0.0074 (3)	−0.0027 (7)	−0.0005 (7)	−0.0039 (6)
P(4)	0.4590 (5)	0.3103 (3)	0.0947 (4)	0.0107 (4)	0.0031 (2)	0.0080 (3)	−0.0012 (6)	−0.0034 (7)	0.0001 (5)
P(5)	0.0098 (4)	0.4023 (4)	0.1738 (3)	0.0096 (4)	0.0057 (3)	0.0026 (1)	−0.0005 (6)	0.0014 (5)	−0.0013 (4)
P(6)	0.0756 (5)	0.3757 (4)	0.3449 (4)	0.0137 (5)	0.0062 (3)	0.0055 (2)	0.0005 (7)	−0.0088 (6)	0.0027 (5)
P(7)	0.0350 (4)	0.5579 (4)	0.2774 (4)	0.0093 (4)	0.0059 (3)	0.0075 (3)	−0.0075 (6)	−0.0046 (7)	−0.0008 (6)
P(8)	−0.1428 (4)	0.4297 (4)	0.3062 (4)	0.0066 (3)	0.0058 (3)	0.0078 (3)	0.0018 (6)	0.0045 (6)	0.0021 (6)
N(1)	0.6170 (9)	0.1489 (9)	0.1558 (9)	0.0025 (8)	0.0051 (7)	0.0075 (8)	0.001 (1)	−0.004 (1)	0.002 (2)
N(2)	0.4214 (10)	0.0956 (9)	0.1271 (9)	0.0075 (11)	0.0039 (7)	0.0068 (9)	−0.003 (2)	−0.000 (2)	0.000 (1)
N(3)	0.4623 (10)	0.2557 (10)	0.1844 (9)	0.0071 (9)	0.0056 (8)	0.0056 (7)	−0.006 (2)	−0.005 (2)	−0.004 (1)
N(4)	0.5664 (14)	0.1299 (13)	0.0022 (13)	0.0106 (16)	0.0102 (13)	0.0129 (15)	0.001 (3)	−0.002 (3)	0.006 (3)
N(5)	0.5865 (10)	0.2920 (9)	0.0653 (8)	0.0072 (9)	0.0087 (9)	0.0052 (7)	−0.007 (2)	0.007 (1)	0.008 (1)
N(6)	0.3921 (10)	0.2394 (11)	0.0371 (11)	0.0090 (10)	0.0056 (8)	0.0079 (8)	−0.000 (2)	−0.011 (2)	0.004 (2)
N(7)	0.0823 (9)	0.3498 (9)	0.2425 (9)	0.0039 (8)	0.0059 (8)	0.0061 (8)	0.004 (2)	0.006 (1)	−0.002 (1)
N(8)	0.0388 (10)	0.5064 (9)	0.1849 (9)	0.0069 (10)	0.0072 (9)	0.0060 (8)	−0.009 (2)	0.006 (1)	0.005 (1)
N(9)	−0.1056 (1)	0.3901 (9)	0.2137 (9)	0.0093 (12)	0.0036 (7)	0.0055 (7)	−0.002 (2)	−0.002 (2)	−0.001 (1)
N(10)	0.1048 (14)	0.4884 (11)	0.3359 (11)	0.0143 (16)	0.0062 (10)	0.0082 (10)	−0.011 (2)	−0.009 (2)	0.005 (2)
N(11)	−0.0410 (10)	0.3772 (9)	0.3649 (7)	0.0077 (9)	0.0051 (7)	0.0032 (5)	0.005 (2)	0.009 (1)	0.004 (1)
N(12)	−0.0916 (12)	0.5349 (8)	0.3024 (10)	0.0125 (14)	0.0015 (5)	0.0065 (8)	0.002 (2)	−0.000 (2)	0.000 (1)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
C(1)	0.688 (2)	0.072 (2)	0.168 (2)	8.8 (7)	C(7)	0.194 (2)	0.326 (2)	0.217 (2)	10.3 (8)
C(2)	0.313 (2)	0.062 (1)	0.156 (1)	7.3 (6)	C(8)	0.004 (2)	0.578 (2)	0.126 (2)	10.7 (8)
C(3)	0.497 (1)	0.312 (1)	0.260 (1)	5.1 (4)	C(9)	−0.167 (2)	0.304 (1)	0.189 (1)	8.0 (6)
C(4)	0.602 (2)	0.056 (2)	−0.048 (2)	8.6 (7)	C(10)	0.175 (2)	0.538 (1)	0.394 (1)	7.1 (6)
C(5)	0.631 (2)	0.361 (2)	0.014 (1)	8.9 (7)	C(11)	−0.080 (2)	0.299 (2)	0.424 (2)	8.5 (6)
C(6)	0.305 (2)	0.269 (2)	−0.012 (1)	8.6 (6)	C(12)	−0.152 (2)	0.594 (2)	0.362 (1)	7.6 (6)

[a] The figures in parentheses are the estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Positional and Thermal Parameters[a,b] for Monoclinic $SP_4(NMe)_6$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	0.7086 (4)	0.4150 (4)	0.1295 (8)	0.0087 (4)	0.0083 (4)	0.044 (1)	0.0051 (7)	0.008 (1)	−0.009 (1)
P(1)	0.8131 (3)	0.3416 (3)	0.0711 (5)	0.0059 (3)	0.0041 (3)	0.0188 (8)	−0.0000 (6)	0.0024 (8)	−0.0022 (9)
P(2)	0.3684 (3)	0.3498 (3)	0.4453 (6)	0.0077 (3)	0.0033 (2)	0.0164 (7)	0.0009 (6)	0.0041 (8)	−0.0001 (9)
P(3)	0.0070 (3)	0.2626 (3)	0.2097 (6)	0.0060 (3)	0.0053 (3)	0.0167 (8)	−0.0017 (6)	−0.0012 (9)	0.0031 (10)
P(4)	0.4567 (3)	0.1640 (4)	0.3483 (5)	0.0076 (3)	0.0054 (3)	0.0170 (8)	0.0031 (6)	0.0055 (9)	−0.0034 (9)
N(1)	0.2849 (8)	0.2730 (10)	0.506 (1)	0.0041 (7)	0.0061 (9)	0.015 (2)	0.003 (1)	0.003 (2)	−0.000 (3)
N(2)	0.9044 (9)	0.3298 (8)	0.231 (1)	0.0071 (9)	0.0032 (8)	0.013 (2)	−0.001 (2)	0.000 (2)	−0.003 (3)
N(3)	0.3599 (9)	0.1112 (9)	0.419 (1)	0.0063 (9)	0.0043 (8)	0.015 (2)	0.000 (2)	−0.003 (3)	−0.002 (3)
N(4)	0.9577 (10)	0.1561 (9)	0.121 (1)	0.0087 (10)	0.0032 (8)	0.016 (2)	−0.000 (2)	−0.003 (3)	0.000 (3)
N(5)	0.4132 (10)	0.2793 (9)	0.307 (2)	0.0093 (10)	0.0027 (8)	0.021 (3)	0.001 (2)	0.009 (3)	0.005 (2)
N(6)	0.5345 (9)	0.1772 (10)	0.539 (1)	0.0054 (9)	0.0057 (9)	0.017 (2)	0.003 (2)	0.005 (2)	−0.001 (3)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
C(1)	0.717 (1)	0.172 (1)	0.099 (2)	5.3 (4)	C(4)	−0.018 (1)	0.068 (1)	0.225 (2)	5.6 (4)
C(2)	0.932 (1)	0.419 (1)	0.344 (2)	5.6 (4)	C(5)	0.415 (1)	0.320 (1)	0.133 (2)	5.8 (4)
C(3)	0.292 (1)	0.067 (1)	0.265 (2)	6.7 (5)	C(6)	0.138 (1)	0.322 (2)	0.027 (2)	7.6 (6)

[a] The figures in parentheses are the estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal parameters is $\exp[(-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

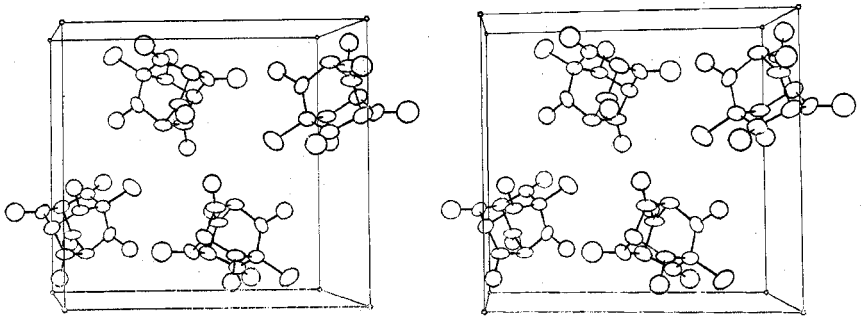


Figure 3. ORTEP stereoview of the unit cell of the monoclinic form.

respectively. Figure 1 shows the molecule and the numbering schemes for all three independent ones as explained in the caption. The thermal vibration ellipsoids shown are those for the molecules numbered S_1, P_1, etc. of the orthorhombic form. Figures 2 and 3 show the molecular packing in the two crystalline forms.

Table IV. Bond Distances (Å) and Bond Angles (deg) in Orthorhombic $SP_4(NMe)_6$[a-c]

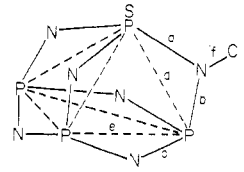
	molecule I	molecule II	average[d]
	Distances		
S-P	1.972 (10)	1.862 (9)	1.92 (5)
P(1,5)-P(2,6)	2.887 (9)	2.963 (8)	
-P(3,7)	2.926 (10)	2.901 (8)	
-P(4,8)	2.954 (9)	2.941 (8)	
SP-P (av)	2.922 (34)	2.935 (31)	2.928 (36)
P(2,6)-P(3,7)	3.015 (7)	2.985 (8)	
-P(4,8)	2.998 (7)	2.950 (7)	
P(3,7)-P(4,8)	3.001 (8)	2.994 (7)	
P-P (av)	3.005 (9)	2.976 (23)	2.991 (22)
P(1,5)-N(1,7)	1.63 (1)	1.65 (1)	
-N(2,8)	1.62 (1)	1.61 (2)	
-N(3,9)	1.69 (2)*	1.61 (1)	
SP-N (av)	1.625 (5)	1.623 (23)	1.624 (16)
P(2,6)-N(1,7)	1.72 (1)	1.73 (1)	
-N(4,10)	1.55 (2)*	1.73 (2)	
-N(5,11)	1.72 (1)	1.51 (1)*	
P(3,7)-N(2,8)	1.73 (1)	1.70 (2)	
-N(4,10)	1.96 (2)*	1.67 (2)	
-N(6,12)	1.70 (2)	1.69 (2)	
P(4,8)-N(3.9)	1.69 (2)	1.70 (1)	
-N(5,11)	1.71 (1)	1.70 (1)	
-N(6,12)	1.66 (2)	1.79 (1)*	
P-N (av)	1.704 (24)	1.703 (21)	1.703 (22)
N(1,7)-C(1,7)	1.47 (2)	1.52 (2)	
N(2,8)-C(2,8)	1.53 (2)	1.52 (3)	
N(3,9)-C(3,9)	1.57 (2)	1.55 (2)	
N(4,10)-C(4,10)	1.44 (3)	1.50 (2)	
N(5,11)-C(5,11)	1.45 (2)	1.60 (2)	
N(6,12)-C(6,12)	1.44 (3)	1.52 (2)	
N-C (av)	1.48 (5)	1.53 (4)	1.50 (6)
	Angles		
S(1,2)-P(1,5)-N(1,7)	112.8 (6)	111.4 (6)	
-N(2,8)	116.3 (7)	118.3 (7)	
-N(3,9)	111.1 (7)	115.0 (6)	
S-P-N (av)	113 (3)	115 (5)	114 (3)
P(1,5)-N(1,7)-P(2,6)	119.5 (7)	122.2 (7)	
-N(2,8)-P(3,7)	121.6 (8)	122.2 (8)	
-N(3,9)-P(4,8)	122.2 (8)	125.2 (8)	
P(2,6)-N(4,10)-P(3,7)	117.8 (13)	122.8 (9)	
-N(5,11)-P(4,8)	122.0 (7)	126.3 (7)	
P(3,7)-N(6,12)-P(4,8)	127.0 (10)	124.0 (8)	
P-N-P (av)	122 (3)	124 (2)	123 (3)
C(1,7)-N(1,7)-P(1,5)	120 (1)	116 (1)	
-P(2,6)	106 (1)	111 (1)	
C(2,8)-N(2,8)-P(1,5)	119 (1)	123 (1)	
-P(3,7)	110 (1)	104 (1)	
C(3,9)-N(3,9)-P(1,5)	113 (1)	116 (1)	
-P(4,8)	116 (1)	113 (1)	
C(4,10)-N(4,10)-P(2,6)	124 (2)	124 (1)	
-P(3,7)	114 (2)	112 (1)	
C(5,11)-N(5,11)-P(2,6)	118 (1)	115 (1)	
-P(4,8)	115 (1)	115 (1)	
C(6,12)-N(6,12)-P(3,7)	112 (1)	121 (1)	
-P(4,8)	122 (1)	109 (2)	
C-N-P (av)	116 (5)	115 (6)	115 (5)
N(1,7)-P(1,5)-N(2,8)	108.9 (8)	104.7 (8)	
-N(3,9)	101.6 (7)	99.9 (7)	
N(2,8)-P(1,5)-N(3,9)	104.9 (7)	105.6 (7)	
N(1,7)-P(2,6)-N(4,10)	106.6 (9)	97.1 (8)	
-N(5,11)	100.0 (10)	102.3 (8)	
N(4,10)-P(2,6)-N(5,11)	108.3 (10)	105.2 (6)	
N(2,8)-P(3,7)-N(4,10)	98.3 (8)	102.8 (9)	
-N(6,12)	100.2 (8)	98.7 (7)	
N(4,10)-P(3,7)-N(6,12)	100.1 (8)	103.6 (8)	
N(3,9)-P(4,8)-N(5,11)	102.7 (8)	97.6 (6)	
-N(6,12)	101.6 (7)	100.7 (7)	
N(5,11)-P(4,8)-N(6,12)	98.3 (7)	98.5 (7)	
N-P-N (av)	103 (4)	101 (3)	102 (4)

[a] Numbers in parentheses are esd's occurring in the last significant figure. [b] Numbers marked * were omitted in computing averages and their esd's. [c] All angles have esd's of 1°. [d] $\sigma = [\Sigma(x_i - \bar{x})^2/(N-1)]^{1/2}$.

Table V. Bond Distances (Å) and Angles (deg) in Monoclinic $P_4S(NCH_3)_6$

	Distances		
P(1)-S	1.919 (5)	P(3)-N(2)	1.757 (10)
P(1)-P(2)	2.961 (5)	P(3)-N(4)	1.708 (10)
P(1)-P(3)	2.963 (5)	P(3)-N(6)	1.692 (10)
P(1)-P(4)	2.943 (5)	P(4)-N(3)	1.735 (11)
P(2)-P(3)	3.007 (5)	P(4)-N(5)	1.703 (10)
P(2)-P(4)	2.998 (5)	P(4)-N(6)	1.703 (10)
P(3)-P(4)	2.992 (5)	N(1)-C(1)	1.52 (2)
P(1)-N(1)	1.675 (11)	N(2)-C(2)	1.52 (2)
P(1)-N(2)	1.638 (10)	N(3)-C(3)	1.53 (2)
P(1)-P(3)	1.621 (10)	N(4)-C(4)	1.46 (2)
P(2)-N(1)	1.718 (10)	N(5)-C(5)	1.49 (2)
P(2)-N(4)	1.697 (10)	N(6)-C(6)	1.49 (2)
P(2)-N(5)	1.674 (10)		
	Angles		
P(2)-P(1)-P(3)	61.01 (12)	N(4)-P(3)-N(6)	103.0 (5)
P(2)-P(1)-P(4)	61.04 (13)	N(3)-P(4)-N(5)	99.7 (5)
P(3)-P(1)-P(4)	60.88 (12)	N(3)-P(4)-N(6)	100.1 (5)
P(1)-P(2)-P(3)	59.52 (12)	N(5)-P(4)-N(6)	102.8 (5)
P(1)-P(2)-P(4)	59.18 (12)	P(1)-N(1)-P(2)	121.5 (6)
P(3)-P(2)-P(4)	59.77 (11)	P(1)-N(2)-P(3)	121.5 (6)
P(1)-P(3)-P(2)	59.46 (12)	P(1)-N(3)-P(4)	122.5 (6)
P(1)-P(3)-P(4)	59.23 (12)	P(2)-N(4)-P(3)	124.1 (6)
P(2)-P(3)-P(4)	59.97 (12)	P(2)-N(5)-P(4)	125.2 (6)
P(1)-P(4)-P(2)	59.78 (13)	P(3)-N(6)-P(4)	123.6 (6)
P(1)-P(4)-P(3)	59.89 (12)	P(1)-N(1)-C(1)	116.6 (8)
P(2)-P(4)-P(3)	60.26 (12)	P(2)-N(1)-C(1)	111.4 (8)
S-P(1)-N(1)	114.6 (4)	P(1)-N(2)-C(2)	117.2 (8)
S-P(1)-N(2)	113.4 (4)	P(3)-N(2)-C(2)	110.4 (8)
S-P(1)-N(3)	114.7 (4)	P(1)-N(3)-C(3)	117.7 (9)
N(1)-P(1)-N(2)	104.8 (5)	P(4)-N(3)-C(3)	109.0 (8)
N(1)-P(1)-N(3)	104.4 (5)	P(2)-N(4)-C(4)	118.7 (8)
N(2)-P(1)-N(3)	103.9 (5)	P(3)-N(4)-C(4)	116.1 (8)
N(1)-P(2)-N(4)	100.8 (5)	P(2)-N(5)-C(5)	118.1 (8)
N(1)-P(2)-N(5)	101.5 (5)	P(4)-N(5)-C(5)	116.7 (8)
N(4)-P(2)-N(5)	101.3 (6)	P(3)-N(6)-C(6)	115.4 (9)
N(2)-P(3)-N(4)	101.8 (5)	P(4)-N(6)-C(6)	114.9 (8)
N(2)-P(3)-N(6)	98.3 (5)		

Table VI. Average Values[a] for Bond Lengths (Å) and Angles (deg) Based on Molecular Symmetry C_{3v}



	orthorhombic	monoclinic	mean
P-S	1.92 (5)	1.919 (5)	1.92 (1)
a	1.624 (16)	1.645 (27)	1.63 (2)
b	1.712 (20)	1.737 (20)	1.73 (2)
c	1.698 (20)	1.696 (12)	1.70 (1)
d	2.928 (36)	2.955 (11)	2.95 (1)
e	2.991 (22)	2.999 (8)	3.00 (1)
f	1.50 (6)	1.50 (3)	1.50 (3)
∠af	118 (3)	117.2 (4)	117 (1)
∠bf	110 (3)	110.3 (8)	110 (1)
∠cc′	117 (4)	116.7 (12)	117 (1)

[a] For all average values $\sigma = [\Sigma(x_i - \bar{x})^2/(N-1)]^{1/2}$.

The molecular dimensions are listed in Table IV for the orthorhombic form and in Table V for the monoclinic form. In Table VI we give average values of the various types of bond lengths that are distinct under the assumption that the molecule has C_{3v} symmetry. These are given for each of the two polymorphs and then for all three of the crystallographically distinct molecules taken together.

The P–S distance, 1.92 (1) Å, is essentially the same as those found in the other $S_nP_4(NMe)_6$ (n = 2, 3, 4) molecules.[3,4] There seem to be no published (=N)$_3$P—S distances with which to compare it. It appears from data on X_3PS (X = CH_3,

Cl, F)[11] compounds that P–S distances are a function of the properties of the X groups depending perhaps on electronegativity and/or π-bonding ability. Since the order of electronegativities of C, N, and Cl varies wildly[12] with the method by which they are estimated, it is questionable whether the position of the present P–S distance (between 1.940 (2) Å for X = CH_3 and 1.885 (5) Å for X = Cl) is understandable on the basis of electronegativities alone or not. According to Pauling-type electronegativities (C, 2.55; N, 3.04; Cl, 3.16) there is at least a qualitative correlation.

The most interesting structural feature is the variation in P–N distances. It will be recalled that the 24 chemically equivalent P–N distances for $P_4(NMe)_6$ in the two crystallographically distinct molecules[3] have a mean value of 1.695 (12) Å. In the $SP_4(NMe)_6$ molecule (see Table VI) there are three chemically distinct sorts of P–N distance. For each type the mean values obtained in the two polymorphs agree quite well. It is found that type c (Table VI), which corresponds to the type present exclusively in $P_4(NMe)_6$, has the same length, namely, 1.70 (1) Å. Type b may be slightly longer, viz., 1.73 (2) Å, but the errors are such that this cannot be considered at all certain. Those of type a, however, with a mean value of 1.63 (2) Å, can be considered shorter with at least 95% confidence.

We believe that this kind of shortening is certainly to be expected on either, or both, of two grounds. First, the increase in the formal oxidation state of the phosphorus atom when a sulfur atom is attached should lead to a decrease in its covalent radius. Data for the two series PX_3, SPX_3, and OPX_3 (X = F, Cl)[13] suggest that such an effect might account for 0.03–0.04 Å of shortening. Second, polarity in the P–S bond in the sense P^+S^- would tend to increase the amount of π-electron density drawn from the nitrogen atoms to the phosphorus atom. This enhancement of the P–N π-bond order would also shorten the P–N bond. At present we shall not try to evaluate the relative importance of these two possible contributions since this could only be done by using other than structural methods, such as spectra of various sorts and calculations.

One encounters here the same lack of precision in atomic positions as in the cases of $P_4(NMe)_6O_4$ and $P_4(NMe)_6S_4$.[3] This seems to be a general problem, characteristic of this class of compounds, and we attribute it both to the globularity of the molecules—which in the extreme case leads to the existence of a plastic phase, as observed for $P_4(NMe)_6$—and also to the absence of a central atom linking the various P and N atoms together *across* the cage, which therefore can be envisioned as a rather soft, quasi-spherical structure, easily deformed under the action of the crystal packing forces. The crystal packing, shown in Figures 2 and 3, does not show any unusual contacts. Actual calculation of all intermolecular distances <4.0 Å showed none <3.2 Å. This is not inconsistent with attributing molecular distortions to intermolecular contacts since the distortions themselves relieve potentially bad intermolecular contacts.

Acknowledgment. We thank the Robert A. Welch Foundation (TAMU) and the CNRS (Nice) for support and NATO for a grant to facilitate our collaboration.

Registry No. $SP_4(NCH_3)_6$, 38448-57-6.

Supplementary Material Available: Listings of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Texas A&M University. (b) Laboratoire de Chimie Minerale Moleculaire.
(2) F. A. Cotton, J. M. Troup, F. Casabianca, and J. G. Riess, *Inorg. Chim. Acta*, **11**, 33 (1974).
(3) Part 1: F. Casabianca, F. A. Cotton, J. G. Riess, C. E. Rice, and B. R. Stults, *Inorg. Chem.*, **17**, 3232 (1977).
(4) Part 3: F. A. Cotton, J. G. Riess, C. E. Rice, and B. R. Stults, *Inorg. Chem.*, to be submitted for publication.
(5) Part 4: F. A. Cotton, J. G. Riess, and B. R. Stults, to be submitted for publication.
(6) A. Wolff and J. G. Riess, *Bull. Soc. Chim. Fr.*, 1587 (1973); F. Casabianca, A. A. Pinkerton, and J. G. Riess, *Inorg. Chem.*, **16**, 864 (1977).
(7) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organomet. Chem.*, **50**, 227 (1973).
(8) Computer programs used on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas, were those of the Enraf-Nonius structure determination package.
(9) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2B.
(10) D. T. Cromer, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.3.1.
(11) K. Karakida and K. Kuchitsu, *Inorg. Chim. Acta*, **16**, 29 (1976).
(12) A *different* position for nitrogen is obtained in *each* of the following cases: Allred-Rochow, N > Cl > C; Pauling, Cl > N > C; Mulliken, Cl > C > N. Cf. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley, New York, 1972, p 115.
(13) T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, **10**, 344 (1971).

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843

A Binuclear Tantalum Compound Containing Bridging 1,2-Dimethyl-1,2-diimidoethene Formed by Dimerization of Acetonitrile

F. ALBERT COTTON* and WILLIAM T. HALL

Received June 12, 1978

It has been shown that a compound previously reported as $[TaCl_3(CH_3CN)_2]_2$ can be recrystallized from tetrahydrofuran (THF) to give $[TaCl_3(THF)_2]_2(=NC(CH_3)=C(CH_3)N=)$. The crystal structure shows a centrosymmetric molecule with octahedrally coordinated tantalum atoms, $TaCl_3(THF)_2(=N-)$, bridged by an ethylene derivative formed by dimerization of CH_3CN. This compound can be treated with CH_3CN to regenerate the starting material, thus implying that the latter is actually $[TaCl_3(CH_3CN)_2]_2(=NC(CH_3)=C(CH_3)N=)$, as suggested by McCarley. The structure found here is analogous to the one reported by McCarley for a niobium analogue. The characteristic crystallographic parameters are space group $P\bar{1}$, a = 7.764 (3) Å, b = 13.910 (3) Å, c = 7.412 (2) Å, α = 88.42 (2)°, β = 98.33 (3)°, γ = 103.27 (3)°, V = 770.9 (4) Å^3, and Z = 1.

The work reported here represents the somewhat unexpected outcome of an attempt we made to characterize potential starting materials for the synthesis of some organotantalum compounds. In 1972 Kepert and co-workers reported a substance to which they assigned the formula $[TaCl_3(CH_3CN)_2]_2$ and for which they proposed a structure incorporating a double bond between the metal atoms. The possibility of this latter structural feature focused our interest on this particular compound and we considered it worthwhile to determine its crystal structure. No suitable crystals were

 © 1978 American Chemical Society