

binuclear monoprotonated species $[\text{Cu}_2\text{LH}]^{5+}$ to form more protonated species, $[\text{Cu}_2\text{LH}_2]^{6+}$ and $[\text{Cu}_2\text{LH}_3]^{7+}$, are similar: 3.17 and 3.27 log units. Such a behavior can be explained assuming that the protonation sites in the complexes are far away and do not influence each other. As already found for other polyazacycloalkanes,^{3,4} macrocycle L forms very stable binuclear hydroxo species $[\text{Cu}_2\text{LOH}]^{3+}$, as shown by the equilibrium constant for the addition of the hydroxide ion to the binuclear complex: $\log K = 3.94$.

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Registry No. A, 55442-07-4; B, 112-24-3; C, 106471-25-4; D, 106471-26-5; E, 112-57-2; F, 99142-42-4; H, 106471-27-6; L, 57970-53-3; $\text{Cu}_2\text{L}(\text{ClO}_4)_4$, 106471-29-8.

Supplementary Material Available: Table of the initial conditions of the potentiometric measurements and computer output of the program SUPERQUAD giving individual data points for emf measurements (25 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Synthesis of Two New 1,3,2,4-Diazadiphosphetidine-Based Phosphazane Oligomers: $[(\text{PhNH})\text{P}_2(\text{NPh})_2]_2\text{NPh}$ and $[(\text{PhNH})\text{PNPh}]_3$

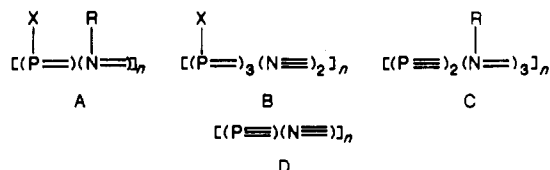
Martin L. Thompson,^{1a} Abbas Tarassoli,^{1b} R. Curtis Haltiwanger, and Arlan D. Norman*

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The synthesis of $[(\text{PhNH})\text{P}_2(\text{NPh})_2]_2\text{NPh}$ (**5**) and $[(\text{PhNH})\text{PNPh}]_3$ (**6**), 1,3,2,4-diazadiphosphetidine-based members of new P(III) phosphazane oligomer/polymer series, are reported. **5** is the final product and **6** is an intermediate in the PCl_3 - PhNH_2 reaction. **5** and **6** have been characterized by spectral (¹H and ³¹P NMR, IR, and MS) data; **5** has been characterized by single-crystal X-ray crystallography. The monosolvate **5**·CS₂ is monoclinic, space group $P2_1/c$, $a = 15.297$ (2) Å, $b = 18.598$ (3) Å, $c = 15.480$ (2) Å, $\beta = 102.6$ (1)°, $Z = 4$, $d_{\text{calcd}} = 1.30$ g/cm³, $d_{\text{obsd}} = 1.30$ g/cm³ (24 °C, Mo Kα). **5**·CS₂ refined to $R_F = 0.069$ and $R_{wF} = 0.083$ for 2930 independent observed reflections. **5** has distorted C_{2v} symmetry in the solid and consists of two cis 1,3,2,4-diazadiphosphetidine (P_2N_2) rings bonded at phosphorus by a bridging PhN group and with PhNH- substitution at terminal P_2N_2 phosphorus atoms. The PCl_3 - PhNH_2 reaction involves stepwise formation of $(\text{PhNH})_3\text{P}$, $[(\text{PhNH})_2\text{P}]_2\text{NPh}$, $[(\text{PhNH})\text{PNPh}]_2$ (**7**), and $[(\text{PhNH})\text{PNPh}]_3$ (**6**) enroute to the dinuclear $[(\text{PhNH})\text{P}_2(\text{NPh})_2]_2\text{NPh}$ (**5**). The mechanisms of phosphazane oligomer formation and interconversion and implications of these for higher phosphazane syntheses are discussed.

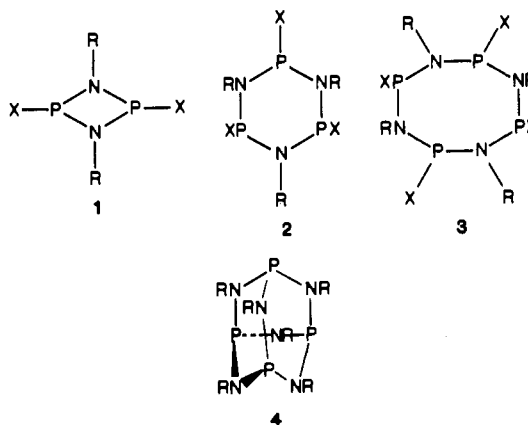
Introduction

The synthesis and properties of new inorganic macromolecules is of considerable current interest.²⁻⁴ Although a variety of systems are known and being studied actively,² glaringly absent are examples of phosphorus(III) polyphosphazanes. These could involve P and N atoms with connectivities to other skeleton atoms of 2:2 (A), 2:3 (B) or 3:2 (C), or 3:3 (D); however, except for

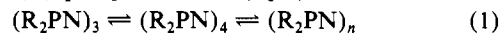


phosphorus nitride $(\text{PN})_n$,³⁻⁵ other P(III) polyphosphazanes are not well characterized.

Reactions that might be expected to yield P(III) polyphosphazanes generally yield four-membered-ring 1,3,2,4-diazadiphosphetidines (**1**),⁶⁻⁸ however with relatively small R groups (R = Me, Et), six- and eight-membered-ring products (**2-4**)^{7,9-13}



have been obtained. The cyclic phosphazanes (**1-3**) and $(\text{RN})_6\text{P}_4$ cages (**4**; R = Me, Et),^{14,15} although not macromolecular, are oligomer members in classes A and C, respectively. Surprisingly, examples of interconversion between series oligomer members, as occurs in P(V) phosphazenes^{2,16} (eq 1), are not common.



Apparently, four-, six-, or eight-membered rings are generally kinetically and possibly thermodynamically favored over linear oligomers or polymers.

Recently, we undertook studies of the syntheses, mechanisms of formation, and structures of P(III) phosphazanes to determine under what conditions routes to large ring or linear phosphazane macromolecules might be found. Systems that appeared particularly interesting were those based on $\text{PhN}=\text{}$ and $\text{P}=\text{}$ bonding

- (1) Permanent address: (a) Lake Forest College, Lake Forest, IL 60045. (b) Shahid Chamran University, Ahwaz, Iran.
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units because from the literature it is clear these systems are complex, involve different products upon variation in reaction conditions, and were not adequately understood. For example, the 1,3,2,4-diazadiphosphetidine $[(\text{PhNH})\text{PNPh}]_2$ (**1**; X = PhNH, R = Ph) claimed to be the product of $(\text{PhNH})_3\text{P}$ thermolysis, or $\text{PCl}_3\text{-PhNH}_2$, $\text{Et}_2\text{NPCl}_2\text{-PhNH}_2$, $[(\text{PhNH})\text{PCl}]_2\text{-PhNH}_2$, or $(\text{Et}_2\text{N})_3\text{P-PhNH}_2$ reactions, is reported to have melting points ranging from 144 to 253 °C.¹⁷⁻²⁴ We have now studied in detail the $\text{PCl}_3\text{-PhNH}_2$ reactions and isolated first members of new 1,3,2,4-diazadiphosphetidine-based oligomer series. The results of our work are described below. Preliminary reports have been published previously.^{25,26}

Experimental Section

Apparatus and Materials. All inert-atmosphere manipulations were carried out in N_2 -flushed glovebags or standard Schlenk-type glassware.²⁷ Thin-layer chromatographic separations were carried out on silica-gel plates (Brinkman Instruments, Model 60F-254). Infrared, ^1H NMR (90.0 MHz), and mass spectral data were obtained by using Perkin Elmer 337G, Varian EM 390, and Varian MAT CH-5 spectrometers, respectively. ^{31}P NMR spectra at 40.5 and 101.2 MHz were obtained with JEOL-PFT100 and Bruker WM-250 spectrometers, respectively. ^1H NMR and ^{31}P NMR chemical shifts were measured relative to internal $(\text{CH}_3)_4\text{Si}$ and H_3PO_4 , respectively; $+\delta$ values are downfield from the standard. Simulation of second-order NMR spectra²⁸ was accomplished by using a Nicolet Series 1080 nuclear magnetic resonance spectrum calculation program, NMRCAL NIC 8015-71170, from Nicolet Instruments, Inc., Madison, WI. Single-crystal X-ray data were collected at ambient temperature by using a Nicolet PI automated diffractometer (graphite monochromator). Elemental analyses were done by Huffman Analytical Laboratories, Wheatridge, CO.

Phosphorus trichloride (K & K Laboratories) was distilled before use. PhNH_2 (Mallinckrodt Chemical Works) was distilled from CaH_2 and stored over molecular sieves. S_8 (sublimed, K & K Laboratories) was purified routinely. Benzene and toluene were distilled from Na/K alloy. Chloroform, CS_2 , and CH_2Cl_2 were distilled from P_4O_{10} immediately before use. Benzene is carcinogenic and should be handled with extreme care.

$[(\text{PhNH})\text{P}_2(\text{NPh})_2]_2\text{NPh}$ (5**).** Typically, PCl_3 (0.20 mol) in toluene was added slowly under N_2 to a stirred solution of PhNH_2 (0.95 mol) in toluene at 0 °C. The reaction mixture was warmed slowly to 25 °C. After 2 h at reflux, PhNH_2Cl was filtered from the cooled reaction mixture. ^{31}P NMR spectral analysis of the filtrate showed **5** and small quantities (ca. 5–10%) of $[(\text{PhNH})\text{PNPh}]_3$ (**6**) (δ 109.6, 106.9, 62.0) and $[(\text{PhNH})\text{PNPh}]_2$ (**7**) (δ 104.0). Evaporation of the filtrate to dryness in vacuo and recrystallization from CH_2Cl_2 yielded pure $[(\text{PhNH})\text{P}_2(\text{NPh})_2]_2\text{NPh}$ (**5**) as a monosolvate (mp 249–252 °C; 85% yield). Anal. Calcd for $\text{C}_{42}\text{N}_7\text{P}_4\text{H}_{37}\text{-CH}_2\text{Cl}_2$, C, 60.86, N, 11.56; H, 4.63; P, 14.60; Cl, 8.36. Found: C, 61.12; N, 11.74; H, 4.51; P, 41.30; Cl, 7.90. Recrystallization from CS_2 yielded **5** as the CS_2 monosolvate. Anal. Calcd for $\text{C}_{42}\text{N}_7\text{P}_4\text{H}_{37}\text{-CS}_2$; C, 61.49; N, 11.68; H, 4.44; P, 14.76. Found: C, 62.00; N, 11.58; H, 4.49; P, 14.59. **5** is soluble in C_6H_6 , CH_2Cl_2 , CHCl_3 , toluene, and CS_2 and slightly soluble in $(\text{C}_2\text{H}_5)_2\text{O}$. IR ($5\text{-CH}_2\text{Cl}_2$, KBr pellet): 3340 (s), 3010–3090 (complex, m), 1600 (vs), 1490 (vs), 1370 (s), 1340 (m), 1315 (w), 1270 (vs), 1220 (s), 1180 (s), 1150 (m), 1105 (m), 1075 (s), 1028 (s), 997 (s), 970 (w), 845–910 (broad, vs), 790 (s), 745 (vs), 690 (vs), 613 (m), 550 (s), 420 (m) cm^{-1} . MS, parent and eight most intense envelopes, m/e (% relative intensity): 763 [4.4; $\text{P}_4\text{-(NC}_6\text{H}_5)_7\text{H}_2^+$], 548 (24.4), 457 (40.0), 428 (35.4), 336 (93.4), 213 (17.1), 122 (100), 93 (35.1), 77 (21.6). ^1H NMR ($5\text{-CH}_2\text{Cl}_2$, CDCl_3): δ

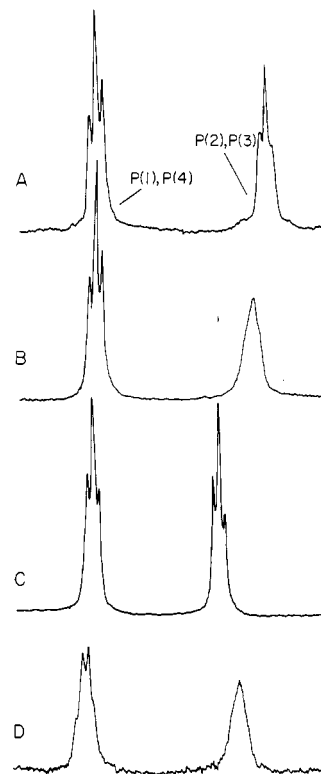


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[(\text{PhNH})\text{P}_2(\text{NPh})_2]_2\text{NPh}$ (**5**): A, in toluene- d_8 at 80 °C; B, in CS_2 /toluene- d_8 at 22 °C; C, in toluene- d_8 at -68 °C; D, ^{31}P NMR (^1H -coupled) spectrum of **5** at 22 °C.

7.64–6.66 (m, area 35, C_6H_5), 3.52 (d, area 2, $^2J_{\text{HP}} = 6.4$ Hz), 5.33 (s, area 2, CH_2Cl_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (10% in CS_2 /toluene- d_8 , 22 °C, 40.5 MHz, Figure 1B): δ 111.8 \pm 0.2 [t, apparent $J = 6.3$ Hz, area 1; P(1)P(4)], 107.6 \pm 0.2 [broad s, area 1, P(2)P(3)]; with ^1H coupling the δ 111.8 resonance collapses to a broad apparent quartet (Figure 1). $^{31}\text{P}\{^1\text{H}\}$ NMR: (10% in toluene- d_8 , 80 °C) δ 112.5, 107.9 (Figure 1A); (10% in CS_2 /toluene- d_8 , -68 °C) δ 109.5, 104.9 (Figure 1C). Simulation of the $^{31}\text{P}\{^1\text{H}\}$ spectrum at -68 °C (AA'XX')²⁸ yields spectral parameters of $^2J_{\text{P}(2)\text{P}(3)} = 3$ Hz, $^2J_{\text{P}(1)\text{P}(2)\text{P}(3)\text{P}(4)} = 6.4$ Hz, and $^4J_{\text{P}(1)\text{P}(3)\text{P}(2)\text{P}(4)} = 7.3$ Hz. Simulation is relatively insensitive to $^2J_{\text{P}(2)\text{P}(3)}$; values of $^2J = 0$ –400 Hz yielded an acceptable fit. The spectrum at 101.5 MHz is essentially identical with that observed at 40.5 MHz.

$[(\text{PhNH})\text{PNPh}]_3$ (6**).** Typically, PCl_3 (0.250 mol) was added dropwise to PhNH_2 (1.50 mol) in CH_2Cl_2 (350 mL) at 0 °C in the apparatus used for preparation of **5**, above. The solution was filtered to remove bulk PhNH_2Cl . The filtrate was evaporated to dryness and washed with cold benzene. The solid was redissolved in CH_2Cl_2 and the mixture filtered. ^{31}P NMR spectral analysis showed the solution to contain **6** (ca. 60%), $[(\text{PhNH})\text{PNPh}]_2$ (**7**) (ca. 30%),²⁹ and **5** (ca. 10%). An equal volume of n -hexane was added to the filtrate. The solution upon cooling yielded white fibrous crystals of **6** (mp 185–186 °C; 50–55% yield). Anal. Calcd for $\text{C}_{36}\text{H}_{33}\text{N}_6\text{P}_3$; C, 67.28; H, 5.18; N, 13.06; P, 14.47. Found: C, 67.50; H, 5.22; N, 12.97; P, 14.40. IR (KBr): 3310 (s), 3010 (s), 2580 (w), 2480 (w) 1950 (m), 1930 (m), 1830 (w), 1590 (vs), 1480 (vs), 1390 (sh), 1370 (s), 1340 (m), 1260 (vs), 1220 (vs), 1180 (m), 1160 (m), 1110 (m), 1080 (s), 1030 (s), 1000 (m), 940 (m), 840–910 (vs), 750 (s), 700 (s), 610 (m) cm^{-1} . MS: owing to sample thermolysis, reliable data were not obtained. ^1H NMR (CDCl_3): δ 7.55–6.66 (m, area 30, C_6H_5), 4.43 (area 2, $^2J_{\text{HP}} = 6.5$ Hz, NH), 3.28 (area 1, $^2J_{\text{HP}} = 6.3$ Hz, NH). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8 ; AMX pattern): δ 109.6 [d of d, area 1, $^2J_{\text{P}(2)\text{P}(3)} = 11.9$ Hz, $^2J_{\text{P}(1)\text{P}(2)} = 363$ Hz; P(2)], 106.9 [d, area 1, P(3)], 62.0 [d, area 1, P(1)]; the spectral appearance is independent of temperature in the range -90 to +80 °C.

6 is soluble in C_6H_6 , toluene, CHCl_3 , and CH_2Cl_2 and moderately soluble in hexane and Et_2O .

$[(\text{PhNH})\text{PNPh}]_2$ (7**).** After successive removal of **5** and **6** from **5**, **6** and **7** mixtures (above), crystallization of **7** from mother liquors yielded product highly enriched in **7** (95% **7**, 5% **6**). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene, 22 °C): δ 104.8 (s). ^1H NMR (toluene- d_8): δ 6.98–6.49 (area 24, C_6H_5), 4.51 (area 2, $^2J_{\text{HP}} = 12.3$ Hz, NH). MS, most intense peak in parent

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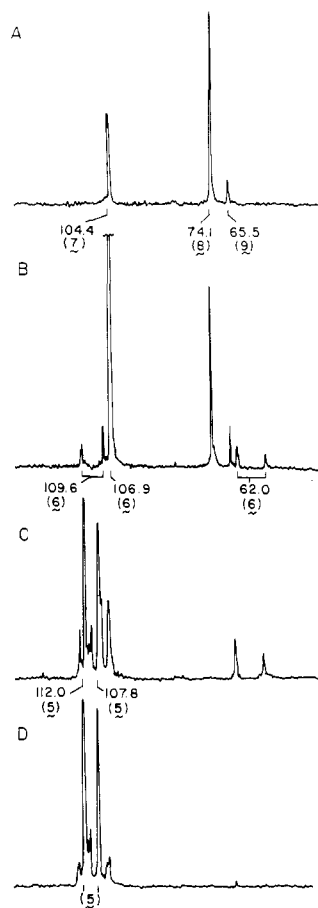


Figure 2. PCl_3 - PhNH_2 reaction series: A, 10% PCl_3 added, 25 °C; B, 25% PCl_3 added, 25 °C; C, 90% PCl_3 added, 25 °C; D, 100% PCl_3 added, 110 °C.

and four most intense envelopes, m/e (% relative intensity): [1; P_2 - $(\text{NC}_6\text{H}_5)_4\text{H}_2^+$], 336 (2), 214 (1), 122 (5), 94 (100).

7 is soluble in CH_2Cl_2 , CHCl_3 , C_6H_6 , and toluene and moderately soluble in Et_2O . 7 shows no decomposition under N_2 during 4 days at 25 °C.

^{31}P NMR Spectral Analysis of PhNH_2 - PCl_3 Reactions. PCl_3 in toluene was added dropwise under N_2 at 0 °C to a stirred solution of PhNH_2 in toluene at 0 °C, in a reactor from which samples could be withdrawn periodically for ^{31}P NMR spectral analysis. Spectra of solutions obtained after filtration of PhNH_3Cl , at several selected reagent ratios, are shown in Figure 2.

Reactions of 5 or 6. 5 after 16-h reflux with excess S_8 in toluene yields a mixture of products (complex ^{31}P NMR spectral resonances between δ 38 and δ 83), which could not be separated; however, no $[(\text{PhNH})\text{P}(\text{S})\text{NPh}]_2$ ³⁰ was observed. 6 with S_8 reacted slowly in toluene at 25 °C to form a complex mixture; $[(\text{PhNH})\text{P}(\text{S})\text{NPh}]_2$ ³⁰ (25% yield) was the only product characterized. Dry O_2 showed essentially no reaction with 5 (<5%) in CH_2Cl_2 at 25 °C. 5 or 6 with $(\text{CH}_3)_3\text{NO}$ underwent no reaction in 12 h in CH_2Cl_2 at 25 °C.

5 and excess PhNH_2 showed no reaction after 4-h reflux in toluene, in both the absence and presence of Et_3N .

5 or 6 with excess $\text{C}_2\text{H}_5\text{OH}$ in CH_2Cl_2 react slowly. ^{31}P NMR spectral analyses of reactions as they progressed showed immediate formation of $(\text{EtO})_3\text{P}^{31}$ and no detectable quantities of intermediate ethanolysis products. Hydrolysis of 5 or 6 occurs slowly; reaction with a deficiency of H_2O in CH_2Cl_2 yields $(\text{PhNH})_2\text{P}(\text{O})\text{H}$ ³² along with other uncharacterized products.

X-ray Structure Analysis of 5. Crystallization of 5 from CH_2Cl_2 or CS_2 yielded crystals of 5- CH_2Cl_2 or 5- CS_2 suitable for X-ray analysis. The crystals were mounted on glass fibers and coated with epoxy resin.

Table I. X-ray Crystallographic Data for $[(\text{PhNH})\text{P}_2(\text{NPh})_2]\text{NPh}$ (5)

	5- CH_2Cl_2	5- CS_2
formula	$\text{P}_4(\text{C}_6\text{H}_5\text{N})_5$ - $(\text{C}_6\text{H}_5\text{NH})_2\cdot\text{CH}_2\text{Cl}_2$	$\text{P}_4(\text{C}_6\text{H}_5\text{N})_5$ - $(\text{C}_6\text{H}_5\text{NH})_2\cdot\text{CS}_2$
fw	839.842	848.636
space group	$P2_1/c$	$P2_1/c$
a , Å ^a	15.414 (5)	15.297 (2)
b , Å	18.668 (8)	18.598 (3)
c , Å	15.389 (6)	15.480 (2)
β , deg	103.6 (1)	102.61 (1)
V , Å ³	4304 (2)	4297 (1)
d_{calcd} , g/cm ³	1.31	1.30
d_{obsd} , g/cm ³	1.32	1.30
Z	4	4
$F(000)$	1760	1744
$\lambda(\text{Mo K}\alpha)$, Å	0.71069	0.71069
cryst size, mm	0.5 × 0.5 × 0.5	0.43 × 0.36 × 0.30
cryst habit	colorless needles	colorless needles
temp, K	292 ± 3	292 ± 3
scan mode	θ - 2θ	θ - 2θ
scan speed, deg min ⁻¹	2.0	variable, 2.0-24.0
scan range, deg	1.1 below $\text{K}\alpha_2$ to 0.9 above $\text{K}\alpha_2$	0.8 below $\text{K}\alpha_1$ to 0.8 below $\text{K}\alpha_2$
2θ limit, deg	2.0-50.0	2.0-40.0
bkgd time/scan time	0.5	0.5
no. of data points:	3947; 2932	3582; 2461
measd; obsd, $F_o^2 > 3.0\sigma(F_o^2)$		
abs cor	none	none
ratio of observns to params	16:1	12:1
R	0.087	0.069
R_w	0.113	0.083
goodness of fit	3.67	2.57

^a Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

Cell parameters were determined on the diffractometer. The two monosolvates are isomorphous. Crystal data, details of data collection, methods of solution, and refinement are summarized in Table I. Data were corrected for Lorentz and polarization effects. The structure of 5- CH_2Cl_2 was solved by using direct methods³³ and refined by using full-matrix least-squares procedures. All calculations were carried out on the dual CDC 6400's at the University of Colorado Computing Center by using significant reflections,³⁴ scattering factors for neutral atoms,³⁵ and program contained in or based on Ibers' Northwestern University Crystallographic Computing Package,³⁶ the Multan 78 package, and Syntex's data reduction routines.

For 5- CH_2Cl_2 , the CH_2Cl_2 showed considerable disorder. After numerous attempted models and cycles of refinement, a model with four overlapping partially occupied sites for the dichloromethane was arrived at. This model refined to the values given in Table I with all nongroup atoms treated anisotropically and hydrogen atoms included in idealized positions.³⁷ These residuals, although not unreasonable given the extent of the disorder of the CH_2Cl_2 molecule, were less than satisfactory. Hence a complete analysis of 5- CS_2 was carried out. Since 5- CS_2 is isomorphous with 5- CH_2Cl_2 , refinement began by using parameters from the latter excluding those for CH_2Cl_2 and for hydrogen atoms. Isotropic refinement based on these parameters converged with $R = 0.19$. The

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(37) The isotropic thermal parameters for the hydrogens were set to be 1 greater than those of the atom to which they were attached.

Table II. Positional Parameters for the Nongroup Atoms of [(PhNH)P₂(NPh)₂]₂NPh-CS₂ (**5**·CS₂)

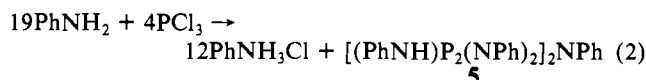
atom	x	y	z	B _{eq} ^a , Å ²
P(1)	0.09093 (18)	0.20909 (12)	-0.00096 (14)	4.54
P(2)	0.06240 (16)	0.07211 (11)	-0.04381 (13)	4.05
P(3)	0.13576 (16)	-0.06099 (11)	-0.09267 (14)	4.00
P(4)	0.27328 (17)	-0.12751 (12)	-0.13262 (15)	4.72
N(1)	0.1929 (5)	0.2382 (3)	-0.0077 (4)	4.8
N(2)	0.0580 (4)	0.1556 (3)	-0.0931 (3)	4.0
N(3)	0.1111 (4)	0.1241 (3)	-0.0448 (4)	4.0
N(4)	0.1491 (4)	0.0297 (3)	0.0776 (4)	3.5
N(5)	0.1797 (4)	-0.0790 (3)	-0.1832 (4)	4.0
N(6)	0.2373 (4)	-0.0971 (3)	-0.0420 (4)	4.0
N(7)	0.3583 (5)	-0.0741 (4)	-0.1396 (5)	5.5
C(1)	-0.3799 (13)	0.3638 (9)	0.0067 (12)	12.1
S(1)	-0.3802 (11)	0.4343 (7)	0.0573 (10)	21.0
S(2)	-0.3773 (10)	0.2982 (6)	-0.0325 (12)	22.2
S(3)	-0.4271 (27)	0.3472 (24)	-0.0906 (19)	20.0
S(4)	-0.362 (4)	0.414 (4)	-0.0783 (18)	24.0

$$^a B_{eq} = (B_{11}B_{22}B_{33})^{1/3}.$$

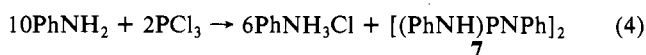
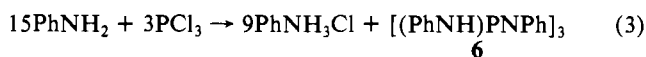
resulting difference map revealed the CS₂ in terms of two partially occupied sites. Least-squares refinements, with nongroup atoms treated anisotropically, group atoms treated isotropically, and hydrogen atoms included in fixed idealized positions with isotropic thermal parameters,³⁷ resulted after further least-squares refinement in the values given in Table I. Final positional parameters for **5**·CS₂ are given in Table II. Thermal and group parameters for **5**·CS₂ and positional, thermal, and group parameters for **5**·CH₂Cl₂ are given in the supplementary material.

Results and Discussion

Phosphorus trichloride and PhNH₂ react readily to form a series of PhNH/PhN-substituted P(III) phosphazanes. The products obtained depend critically upon reaction conditions. At 110 °C in toluene, with a PhNH₂:PCl₃ mole ratio of (4.7–4.9):1.0, the nearly quantitative and final product of reaction is the new dinuclear 1,3,2,4-diazadiphosphetidine [(PhNH)P₂(NPh)₂]₂NPh (**5**) formed as

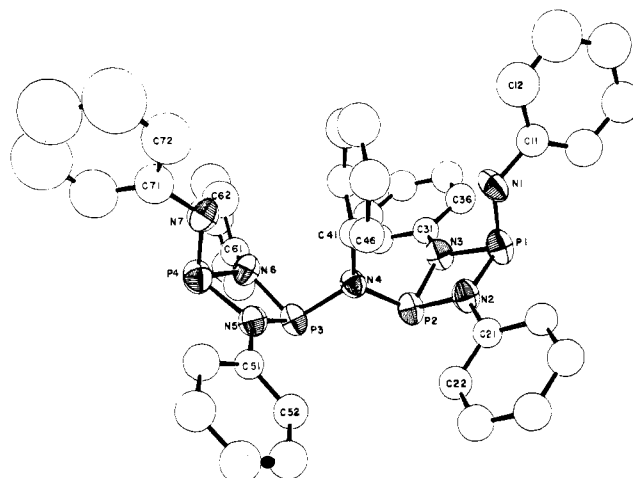


At a slightly higher PhNH₂:PCl₃ ratio ((5.0–5.1):1.0) and lower reaction temperature (25 °C), the main products of reaction are the two- and three-phosphorus phosphazane dimer and trimer oligomers [(PhNH)PNPh]₂ (**7**)¹⁹ and [(PhNH)PNPh]₃ (**6**), according to



Crystalline **5** can be obtained as a CS₂ or CH₂Cl₂ monosolvate, allowing its structure to be determined by X-ray analysis. The structure of **5** along with the numbering scheme used is shown in Figure 3. Intramolecular bond distances and angles are listed in Table III. Compound **5** consists of two, four-membered 1,3,2,4-diazadiphosphetidine (P₂N₂) rings bonded at P(2) and P(3) by a bridging PhN group. Phosphorus atoms P(1) and P(4) contain appended PhNH moieties. The four ring nitrogen atoms, N(1), N(2), N(3), and N(4), are each bonded to a phenyl ring. The mode of substitution at the phosphorus atoms results in a molecule in which each ring is in a cis geometrical isomeric form. Overall, **5** is in the cis-cis form and exhibits distorted C_{2v} molecular symmetry.

The basic structural parameters of **5** are closely similar, insofar as they can be compared, to those reported for other phosphorus(III) 1,3,2,4-diazaphosphetidines.^{7,8,38} The mean P–N ring distance of 1.720 (8) Å is within the 1.68–1.74 Å range expected. These distances are slightly longer than the exo P–N distances

**Figure 3.** Numbering system and ORTEP drawing of [(PhNH)P₂(NPh)₂]₂NPh (**5**). Ellipsoids include 50% of the atom probability. Hydrogen atoms and disordered CS₂ are omitted for clarity.**Table III.** Structural Parameters for [(PhNH)P₂(NPh)₂]₂NPh-CS₂ (**5**·CS₂)

(a) Distances, Å			
P(1)–N(1)	1.676 (8)	P(3)–N(4)	1.709 (6)
P(1)–N(2)	1.722 (6)	P(3)–N(5)	1.715 (6)
P(1)–N(3)	1.732 (6)	P(3)–N(6)	1.716 (7)
P(2)–N(2)	1.725 (6)	P(4)–N(5)	1.728 (7)
P(2)–N(3)	1.710 (6)	P(4)–N(6)	1.711 (7)
P(2)–N(4)	1.719 (7)	P(4)–N(7)	1.659 (8)
N(1)–C(11)	1.400 (8)	N(5)–C(51)	1.404 (7)
N(2)–C(21)	1.407 (7)	N(6)–C(61)	1.418 (8)
N(3)–C(31)	1.406 (7)	N(7)–C(71)	1.387 (11)
N(4)–C(41)	1.430 (9)		
(b) Angles, deg			
N(2)–P(1)–N(3)	78.8 (3)	N(1)–P(1)–N(2)	104.1 (3)
N(2)–P(2)–N(3)	79.3 (3)	N(1)–P(1)–N(3)	103.6 (3)
N(5)–P(3)–N(6)	79.6 (3)	N(4)–P(2)–N(2)	103.7 (3)
N(5)–P(4)–N(6)	79.4 (3)	N(4)–P(2)–N(3)	105.9 (3)
P(1)–N(2)–P(2)	100.2 (3)	N(4)–P(3)–N(5)	104.4 (3)
P(1)–N(3)–P(2)	100.4 (3)	N(4)–P(3)–N(6)	104.8 (3)
P(3)–N(5)–P(4)	99.5 (3)	N(7)–P(4)–N(5)	104.0 (3)
P(3)–N(6)–P(4)	100.1 (3)	N(7)–P(4)–N(6)	104.7 (3)
P(2)–N(4)–P(3)	114.7 (4)		
P(1)–N(1)–C(11)	124.4 (6)	P(3)–N(4)–C(41)	122.7 (5)
P(1)–N(2)–C(21)	129.3 (5)	P(3)–N(5)–C(51)	129.8 (5)
P(2)–N(2)–C(21)	126.6 (5)	P(4)–N(5)–C(51)	126.1 (5)
P(1)–N(3)–C(31)	128.0 (5)	P(3)–N(6)–C(61)	127.5 (5)
P(2)–N(3)–C(31)	130.7 (5)	P(4)–N(6)–C(61)	125.9 (5)
P(2)–N(4)–C(41)	122.5 (5)	P(4)–N(7)–C(71)	125.0 (6)

(1.677 (8) Å) but similar to the bridging PhN group distances (1.714 (8) Å). Also, the mean P–N–P and N–P–N angles of 100.1 (3) and 79.3 (3)° are consistent with those observed previously.

The conformational properties of **5** are of interest and suggest features of the chemistry to be expected. The P₂N₂ rings of **5** are nearly planar; both are bent slightly along N...N axes such that the substituents on phosphorus are bent back away from each other. The [P(1),N(2),N(3)]–[P(2),N(2),N(3)] and [P(3),N(5),N(6)]–[P(4),N(5),N(6)] interplane dihedral angles in **5** are 11.2 and 11.3°, respectively. These angles are smaller than generally observed in alkylamino-substituted 1,3,2,4-diazadiphosphetidines^{7,8} but are in contrast to the arylamino-substituted *cis*-(PCINPh)₂, which is planar.³⁸ It is possible that weak π-bonding effects in aryl-substituted P₂N₂ rings stabilize them in planar form, but this effect is not large enough to overcome the steric repulsions between substituents in exo-ring positions. The ring-bonded phenyl groups (Ph21, Ph31, Ph51) approach coplanarity with the P₂N₂ planes; mean interplane dihedral angles are 15.2°. The Ph61 plane is rotated to 53.5°, probably the result of packing in the crystal. **5** assumes a conformation around the P(3)–N(4) and P(2)–N(4) bonds such that the lone-pair electrons

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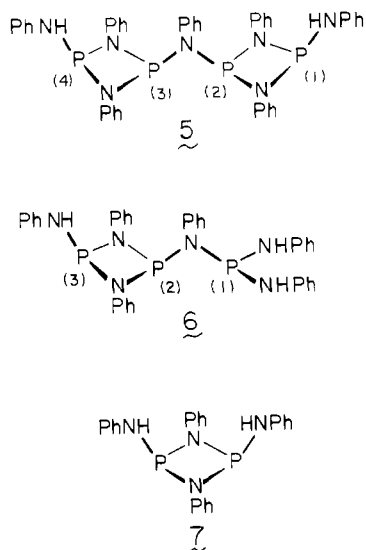


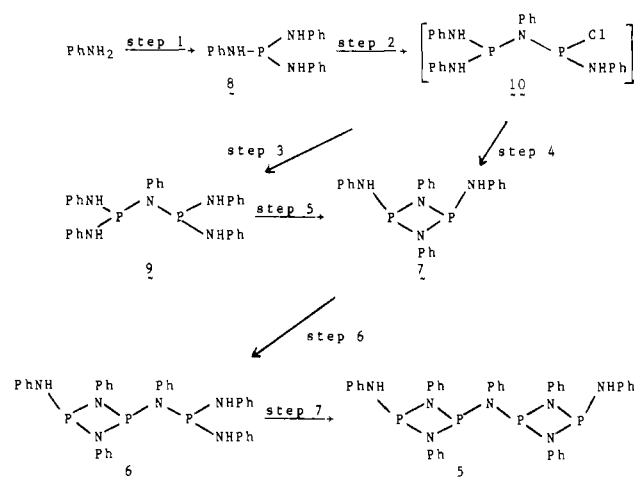
Figure 4. Structures of the 5-7 phosphazane series.

on phosphorus atoms P(2) and P(3) are essentially eclipsed. The dihedral angle between perpendiculars to the [N(2),N(3),N(4)] and [N(3),N(5),N(6)] planes is 6.4° . This angle is surprisingly close to that of 14° observed in the closely related [(PhNH)₂P]₂NPh (9)²⁹ and suggests that 5, like 9,³⁹ could have interesting coordination chemistry.⁴⁰ The eclipsed electron pair conformation is generally seen for those [(X₂N)₂P]₂NR diphosphinoamine systems where the R and X moieties are not exceptionally large.^{41,42}

New compounds 5 and 6 and the previously reported,¹⁹ but incompletely characterized, 7 are also characterized by spectral (¹H and ³¹P NMR, IR, and MS) data. The ¹H NMR spectra of 5, 6, and 7 show characteristic C₆H₅ and NH resonances in ratios of 35:2, 30:3, and 20:2, respectively. 5 and 7 show only one NH resonance each; however, 6 shows two NH resonances in relative areas 2:1 from two PhNH groups of the (PhNH)₂P unit and the one exo PhNH unit, respectively. Phosphorus-31 NMR data show clearly that 5-7 are all cis isomers in solution (Figure 4). The ³¹P chemical shifts of P₂N₂ ring phosphorus atoms fall in the δ 100-120 region, characteristic of cis isomers and well out of the δ 160-190 range for trans isomers.^{8,38} 6 exhibits a resonance at δ 62.0, characteristic of a phosphorus in an acyclic triaminophosphine, e.g. (PhNH)₃P or [(PhNH)₂P]₂NPh.²⁹ Upon ¹H decoupling of the ³¹P NMR spectrum of 5 (Figure 1C), the high-field resonance (δ 107.4) remains unchanged while the low-field resonance (δ 112.8) emerges as a sharp triplet (Figure 1D), allowing assignment of the δ 107.4 and 112.8 resonances to the middle [P(2)P(3)] and terminal [P(1)P(4)] phosphorus atoms. The slight temperature dependence of the spectrum is likely due to ¹⁴N quadrupolar effects and is not the result of changes in conformational populations.^{7,42} Similarly, upon decoupling the ³¹P NMR spectrum of 6 only the δ 109.6 resonance is unaffected. Thus, the δ 109.6 and 106.9 resonances are assigned to phosphorus atoms P(2) and P(3), respectively.

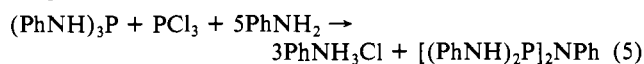
Insight into the sequence by which PhNH₂ and PCl₃ react to form 7, 6, and ultimately 5 is obtained by observing the ³¹P NMR spectrum of PhNH₂-PCl₃ reaction mixtures as a function of added PCl₃. Under these conditions PhNH₂ is always in excess, a situation closely similar to that of the preparative-scale reactions from which 5-7 are best obtained. A typical reaction series is shown in Figure 2. Upon initial addition of PCl₃ (ca. 10%), a

Scheme I

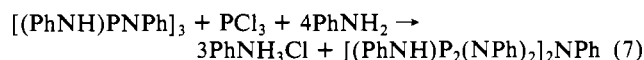
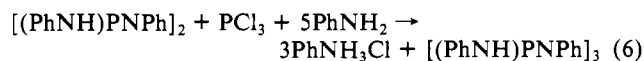


singlet at δ 65.5 and more intense resonances at δ 74.1 and 104.4 appear (Figure 2A). On the basis of our previous studies²⁹ and work herein, we can assign the δ 74.1, 65.5, and 104.4 resonances to (PhNH)₃P (8), the diphosphinoamine, [(PhNH)₂P]₂NPh (9), and [(PhNH)PNPh]₂ (7), respectively. Continued addition of PCl₃ (Figure 2B) causes a marked increase in the δ 104.4 singlet and the appearance of the AMX pattern²⁸ characteristic of 6 at δ 109.6, 106.9, and 62.0. Subsequently (Figure 2C) 6 continues to increase, 5 appears at δ 112.0 and 107.8, and resonances due to 8 and 9 disappear. Finally, after complete addition of PCl₃ (ratio 4.7:1.0) and the reaction is heated to 100 °C, 5 is the near quantitative final product (Figure 3D). In none of the reaction mixtures is evidence for trans species seen. This is in contrast to the situation observed for alkylamino-substituted diazadiphosphetidines, where except for the very bulky *t*-Bu group, both cis and trans isomers are formed and exist in equilibrium.^{7,8} No indication of *cis*-5 or *cis*-6 conversion to trans forms at high temperatures is seen, suggesting strongly that the cis isomers are in fact more thermodynamically stable.

The PhNH₂-PCl₃ reaction sequence is summarized in Scheme I. The overall mechanism of reaction is complex and undoubtedly involves participation of species in concentrations too low to detect. For example, no evidence is obtained for intermediate species PhNHPCl₂ or (PhNH)₂PCl,⁴³ although they likely are involved. The first aminophosphine formed in concentration high enough to detect is 8. The two-phosphorus products, 7 and 9, form next. Since 7 and 9 appear to form independently, we conclude formation of 7 from 9 (step 5) is not a reaction pathway of major importance. Since 7 and 9 appear at the same time in the sequence, they could form from a common intermediate, e.g. 10. 9 could form by PCl₃/PhNH₂ addition to 8 via the chlorodiphosphinoamine 10 (steps 2 and 3) as



7 likely arises from rapid ring closure and HCl elimination from 10 (step 4). The three- and four-phosphorus products, 6 and 5, then form successively by PCl₃/PhNH₂ additions and HCl eliminations from 7 (steps 6 and 7), i.e.



Although conversion of 9 to 6 or 9 to 7 by thermal elimination of PhNH₂ can be considered, these processes are relatively slow^{7,29,44} and likely not major contributors here. Also, direct di-

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merization of **7** to **5** via PhNH_2 elimination seems unlikely since this reaction in independent experiments was found to be very slow and does not yield **5** cleanly.

The observed phosphazane products and the product formation order are consistent with those expected in a series that requires successively decreasing $\text{PhNH}_2:\text{PCl}_3$ ratios. Reactant ratios for formation of **8** and **9** are 6:1 (eq 8) and 5.5:1 (eq 9), respectively.

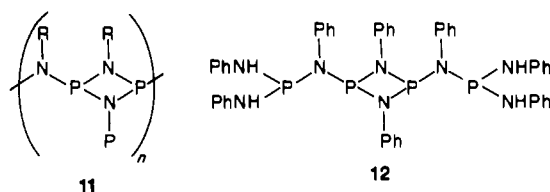


The ideal reactant ratio for oligomers **6** and **7** is 5.0:1.0 (eq 3 and 4), and that for the final product **5** is 4.75:1.0 (eq 2).

Having observed the complexity of the $\text{PCl}_3\text{-PhNH}_2$ reaction product mixture, how sensitive the product distribution is to reaction conditions, and that the final reaction products **6** (or **7**) and **5** have closely similar elemental analytical compositions, we were not surprised that products previously characterized as $[(\text{PhNH})\text{PNPh}]_2$ had widely different properties, especially melting points. On the basis of our data, we conclude that material reported to melt at 145-153 °C was mainly $[(\text{PhNH})\text{PNPh}]_2$ (**7**),¹⁸⁻²⁰ that melting at 249-251 °C was $[(\text{PhNH})\text{P}_2(\text{NPh})_2]_2\text{NPh}$ (**5**),^{17,21} and materials with intermediate melting ranges were mixtures of varying amounts of **5**, **6**, or **7**. Only in one case were ³¹P NMR data reported.²³ Interestingly, a two-resonance pattern like that observed by us for **5** was described; however, the pattern was attributed to a mixture of isomers of **5**.

The 1,3,2,4-diazadiphosphetidines **5**, **6**, and **7** are phosphazanes whose relationships to each other and other phosphazanes is of interest to note: (i) Compound **5** represents the longest oligomeric extension so far of systems based on linked P_2N_2 rings. **5** and **7** can be regarded as the $n = 1$ and $n = 2$ members of diazadiphosphetidine-based series $[(\text{RN})_3\text{P}_2]_n$ (**11**), in which the end

groups are H and PhNH. The known $(\text{RN})_6\text{P}_4$ cages^{14,15} are also



members of this class; however, they can be regarded as nonlinear cluster phosphazanes. The ubiquitous formation of diazadiphosphetidine rings in the higher order condensation products **5** and **6** suggests that perhaps other series of similar P_2N_2 -based oligomer/polymers can be obtained. (ii) Compounds **6** and **7** are two members of a limited oligomeric series of type $[(\text{PhNH})\text{PNPh}]_n$. Monomer ($n = 1$) and tetramer ($n = 4$; **12**) members have not been observed; however, their existence in concentrations too low to detect or as intermediates in interconversion processes cannot be excluded. (iii) Compound **6** is a triphosphazane of formula analogous to that of the previously reported six-membered-ring compound $(\text{PCINMe})_3$ (**2**; X = Cl, R = Me, Et).^{7,11} It is not clear from the studies done so far whether or not **2** is in fact thermodynamically preferred; however, from our studies there seems to be no question that for the Ph-substituted system the P_2N_2 isomer form is thermodynamically preferred.

Acknowledgment. Support of this work by National Science Foundation Grants CHE-7909497 and CHE-8312856 is gratefully acknowledged.

Supplementary Material Available: Tables of anisotropic thermal parameters, rigid-group derived parameters, least-squares planes, equations, and deviations from planes (10 pages); listings of structure factors (17 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Physics and Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1, and Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

Preparation and Crystal Structures of $\text{Hg}_3(\text{NbF}_5)_2\text{SO}_4$, $\text{Hg}_3(\text{TaF}_5)_2\text{SO}_4$, and $\text{Hg}_4(\text{Ta}_2\text{F}_{11})_2$

I. D. Brown,[†] R. J. Gillespie,^{*‡} K. R. Morgan,[‡] J. F. Sawyer,[§] K. J. Schmidt,[‡] Z. Tun,^{†||} P. K. Ummat,[‡] and J. E. Vekris[‡]

Received April 7, 1986

$\text{Hg}_3(\text{NbF}_5)_2\text{SO}_4$ (I) and the isostructural $\text{Hg}_3(\text{TaF}_5)_2\text{SO}_4$ (II) were produced as minor products during the reactions of Hg with SO_2 solutions of $\text{Hg}(\text{MF}_6)_2$ (M = Nb, Ta). Similarly $\text{Hg}_4(\text{Ta}_2\text{F}_{11})_2$ (III) was prepared by the reaction of an SO_2 solution of $\text{Hg}(\text{Ta}_2\text{F}_{11})_2$ with Hg. Crystal data for these compounds are as follows: I [corresponding values for II in brackets], orthorhombic, space group $Fdd2$ with $a = 18.048$ (2) Å [18.078 (7) Å], $b = 15.699$ (2) Å [15.705 (4) Å], $c = 9.166$ (2) Å [9.153 (2) Å], $V = 2597$ (1) Å³ [2599 (2) Å³], $Z = 8$, $D_{\text{exptl}} = 5.485$ (4) g cm⁻³ [6.387 (4) g cm⁻³], $\mu = 37.3$ mm⁻¹ [54 mm⁻¹], $F(000) = 3680$ [4192], $R = 0.048$ [0.109] for 1515 unique [1433] reflections; III, monoclinic, space group $I2/c$, $a = 18.556$ (8) Å, $b = 7.528$ (3) Å, $c = 14.714$ (8) Å, $\beta = 91.72$ (4)°, $V = 2054$ (2) Å³, $Z = 4$, $D_{\text{exptl}} = 6.285$ (5) g cm⁻³, $\mu = 52.9$ mm⁻¹, $F(000) = 3240$, $R = 0.056$ for 1248 unique reflections. Compounds I and II contain nearly linear Hg_3^{2+} ions ($\text{Hg-Hg} = 2.559$ (2) Å (×2); $\text{Hg-Hg-Hg} = 166.6$ (1)°) linked through $\text{Hg}\cdots\text{O}$ interactions (2.28 (1) Å) involving the two terminal oxygen atoms of the $(\text{MF}_5)_2\text{SO}_4^{2-}$ (M = Nb, Ta) anions. The structure of III consists of $\text{Ta}_2\text{F}_{11}^-$ anions and almost linear Hg_4^{2+} cations linked into infinite zigzag chains by a weak interaction ($\text{Hg}\cdots\text{Hg} = 3.033$ (2) Å) between the terminal Hg atoms of symmetry-related cations. Hg-Hg bond lengths in the cation are 2.593 (2) and 2.630 (2) Å.

Introduction

In recent years there has been a considerable increase in our knowledge of the lower oxidation states of Hg. The structure of Hg_3^{2+} was first reported in $\text{Hg}_3(\text{AlCl}_4)_2$ by Ellison, Levy, and

Fung,¹ and a second example in $\text{Hg}_3(\text{AsF}_6)_2$ was reported by Cutforth, Davies, Dean, Gillespie, Ireland, and Ummat.² The existence of the Hg_4^{2+} ion was first reported by Cutforth, Gillespie, and Ireland,³ and the crystal structure of $\text{Hg}_4(\text{AsF}_6)_2$ was later described by Cutforth, Gillespie, Ireland, Sawyer, and Ummat.⁴

[†] Department of Physics, McMaster University.

^{*} Department of Chemistry, McMaster University.

[‡] University of Toronto.

[§] Present address: Department of Physics, University of Edinburgh, Edinburgh, Scotland.

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