

Figure 2. The in-plane and out-of-plane structural parameters for the [Cu(acacP)]₂ molecule; inversion related atoms are indicated by primes.

topologically equivalent ligands,^{8,9} it appeared likely that the copper(I) moieties would be pseudotetrahedral as are most copper(I)-phosphine complexes. On the other hand, the values of $J(^{109}Ag,^{31}P)$ and $J(^{107}Ag,^{31}P)$ of 826 and 718 Hz measured for $[Ag(acacP)]_2^{10}$ are unusually large for tetracoordinated silver(I).¹¹ Our X-ray crystallographic study clarified this situation by demonstrating that 1 possesses a very unusual structure.

A 0.20- \times 0.35- \times 0.35-mm crystal obtained by slow diffusion of methanol into a CH_2Cl_2 solution of 1 with exclusion of air was used for data collection. The space group and cell data are as follows: monoclinic, space group $P2_1/n$ with a = 9.508 (2) Å, b = 14.529 (3) Å, c = 16.001 (5) Å, $\beta = 92.01$ (2)°, V = 2209.2(9) Å³, $d(\text{calcd}) = 1.356 \text{ g cm}^{-3}$, $d(\text{found}) = 1.34 \text{ g cm}^{-3}$, and Z = 2. Three-dimensional diffraction data (a total of 3657 independent reflections having $2\theta(Cu K\alpha) \leq 130^\circ$) were collected on a Syntex P2₁ autodiffractometer by using graphite-monochromated Cu K α radiation. The position for the Cu atom was located by a weighted (E*F) Patterson synthesis. Subsequent difference Fourier maps revealed the positions of all remaining atoms, including all hydrogens. Least-squares refinement to convergence using anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms gave R = 0.0388 and $R_w = 0.0478^{12}$

The structure of 1 consists of two trigonally coordinated copper(I) units¹³ related through the inversion center and bridged by the phenylene fragment of the acacP chelate (Figure 1). The coordination sphere of the copper atom is very nearly planar with the metal atom within 0.0087 (5) Å of the plane containing the PO_2 donor set. The coordination planes of the dimer are parallel since they are inversion related. As indicated in Figure 2, the two in-plane Cu-O distances differ by ~ 0.1 Å while a third, nonbonding oxygen is a further 1.220 Å distant from the metal center.

The present structure is geometrically related to a growing class of bimetallic complexes characterized by cofacially positioned

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coordinatively unsaturated, low-valent metal ions14 ("dimetallophanes").¹⁵ On the basis of synthetic and structural principles illustrated in this work, a range of new homo- and heterobimetallic complexes can now be anticipated by using chemically and topologically equivalent agents.¹⁶

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Synthesis of [(C₆H₅NH)PNC₆H₅]₃: A Participant in a Phosphorus(III)-Nitrogen Compound Trimer-Dimer **Interconversion Reaction**

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Oligomer interconversion reactions of phosphorus(V)-nitrogen compounds are well characterized for cyclo- and linear polyphosphazenes, e.g.,^{2,3}

$$(\mathbf{R}_2 \mathbf{PN})_3 \rightleftharpoons (\mathbf{R}_2 \mathbf{PN})_4 \rightleftharpoons (\mathbf{R}_2 \mathbf{PN})_n \tag{1}$$

Except for the recently reported dimerization of [(CH₃)₃Si]₂N-PNSi(CH₃)₃,⁴ oligomer interconversions of phosphorus(III)-nitrogen compounds have not been observed. We wish to report now the synthesis and characterization of a novel 1,3,2,4-diazadiphosphetidine $[(C_6H_5NH)PNC_6H_5]_3$ (1) and its conversion to $[(C_6H_5NH)PNC_6H_5]_2$ (2) in what appears to be the first example of a trimer-dimer oligomerization among phosphorus(III)-nitrogen compounds.



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⁽¹⁰⁾ The reaction of AgClO₄ with HacacP and Et₃N in acetonitrile af-(10) The reaction of AgCIO₄ with HacaeP and Et₃N in account the an-forded [Ag(acaeP)]₂ as photosensitive cream-colored crystals. Anal. Calcd for C₅₀H₄₈Ag₂O₄P₂: C, 60.60; H, 4.85; P, 6.26. Found: C, 60.25; H, 4.84; P, 6.48. Spectral data: IR (mull) 1571 (s), 1548 (s) cm⁻¹; ¹H NMR (90 MHz, CD₂Cl₂ solution) δ 8.74–6.7 (m, 14 H), 5.7 (s, 1 H), 1.1 (s, 9 H); ³P[¹H] NMR (40.5 MHz, CD₂Cl₂ solution) 3.6 ppm upfield of 85% H₃PO₄ [¹J(¹⁰⁹Ag,³¹P) = 826 Hz, ¹J(¹⁰⁷Ag,³¹P) = 718 Hz]; field desorption Ms, m/z 990 (M⁺).



Figure 1. Molecular structure of $[(C_6H_5NH)PNC_6H_5]_3 \cdot C_2H_5OH$ and labeling of atom positions. Hydrogen atoms omitted for clarity.

Compound 1 is formed in greater than 80% yield from $[(C_6 H_5NH_2P_2NC_6H_5^5$ thermolysis (2 h, 80 °C) in toluene (eq 2) $3[(C_6H_5NH)_2P]_2NC_6H_5 \rightarrow$

$$2[(C_6H_5NH)PNC_6H_5]_3 + 3C_6H_5NH_2$$
 (2)

or from reaction of PCl₃ with $C_6H_5NH_2$ (1:6 mole ratio, 2 h, 0 °C) in methylene chloride (eq 3). Filtration of either reaction

$$3PCl_3 + 15C_6H_5NH_2 \rightarrow 9C_6H_5NH_3Cl + [(C_6H_5NH)PNC_6H_5]_3 (3)$$

mixture, evaporation of solvent in vacuo, and recrystallization from CH_2Cl_2 or benzene yields pure microcrystalline 1 (mp 180–181 °C). Anal. Calcd for C₃₆H₃₃N₆P₃: C, 67.28; H, 5.18; N, 13.08; P, 14.46. Found: C, 66.87; H, 5.17; N, 13.15; P, 14.58. Spectral data for 1: IR (KBr pellet) characteristic NH and PN ring absorptions⁶ at 3160 and 835 cm⁻¹; ¹H NMR (CDCl₃) & 7.55-6.66 (complex multiplet, area 30, phenyl), 4.43 (d, ${}^{2}J_{HP} = 6.5$ Hz, area 2, NH), and 3.50 (d, ${}^{2}J_{HP}$ = 6.3 Hz, area 1, NH); ${}^{31}P$ NMR (${}^{1}H$ decoupled, C₆D₆, relative to H₃PO₄, ABX spectrum⁷) δ -109.6 (P_2) , -106.9 (P_3) , -62.0 (P_1) , ${}^{2}J_{P_1P_2} = 363 \pm 2$ Hz and ${}^{2}J_{P_2P_3} = 12.3 \pm 0.2$ Hz. Compound 1 oxidizes slowly in air and reacts with water to form $C_6H_5NH_2$ and $(C_6H_5NH)_2P(O)H.^8$

Crystallization of 1 from a saturated CH₂Cl₂ solution by dropwise addition of C₂H₅OH yields crystals of monosolvated 1.C₂H₅OH suitable for single-crystal X-ray analysis. Crystal data⁹ for 1·C₂H₅OH are space group C2/c, a = 23.156 (9) Å, b = 14.533 (5) Å, c = 22.243 (8) Å, $\beta = 100.63$ (3)°, V = 7357 (5) Å³, $\rho_{calod} = 1.16$ g/cm³ (Z = 8), $\rho_{obsd} = 1.17$ g/cm³, μ (Mo K α) = 2.04 cm⁻¹. The molecular structure of 1·C₂H₅OH is shown in

Table I. Selected Structural Parameters in $[(C_6H_5NH)PNC_6H_5]_3 \cdot C_2H_5OH^a$

| Bond Lengths, Å | | | |
|------------------|-----------|-----------------|-----------|
| P(1)-N(1) | 1.682 (7) | P(2)-N(5) | 1.712 (8) |
| P(1) - N(2) | 1.690 (8) | P(3) - N(4) | 1.732 (8) |
| P(1) - N(3) | 1.727 (7) | P(3) - N(5) | 1.714 (8) |
| P(2)-N(3) | 1.694 (7) | P(3) - N(6) | 1.675 (8) |
| P(2)-N(4) | 1.720 (8) | C-N (mean) | 1.410 (9) |
| Bond Angles, deg | | | |
| N(1)-P(1)-N(2) | 93.2 (4) | N(4)-P(3)-N(6) | 102.8 (4) |
| N(1)-P(1)-N(3) | 103.8 (4) | N(5)-P(3)-N(6) | 105.1 (4) |
| N(2)-P(1)-N(3) | 103.3 (4) | P(1)-N(3)-P(2) | 115.5 (4) |
| N(3)-P(2)-N(4) | 106.4 (4) | P(1)-N(3)-C(31) | 122.1 (5) |
| N(3)-P(2)-N(5) | 105.5 (4) | P(2)-N(3)-C(31) | 122.3 (5) |
| N(4)-P(2)-N(5) | 79.5 (4) | P(2)-N(4)-P(3) | 99.7 (4) |
| N(4)-P(3)-N(5) | 79.1 (4) | P(2)-N(5)-P(3) | 100.7 (4) |

^a Standard deviations in the least significant figures are given in parentheses.

Figure 1. Significant interatomic bond distances and angles are summarized in Table I.

The structure of 1 consists of a four-membered 1,3,2,4-diazadiphosphetidine ring, with C_6H_5NH - and $(C_6H_5NH)_2P(NC_6H_5)$ moieties attached to rign phosphorus atoms in a cis diposition relative to the nearly planar P_2N_2 ring. The dihedral angle between perpendiculars to planes N(1), N(2), N(3) and N(3), N(4), N(5) is only 10.1°, making the phosphorus lone pair electrons of P(1) and P(2) approximately eclipsed. The principal structural parameters (Table I), distances, mean ring P-N (1.72 Å) and mean N(exo)-P (1.69 Å), and angles, mean ring P-N-P (100°), mean ring N-P-N (79°), ring N-P (exo)-N (105°), P-N(C₆- H_5)-P (115°), are remarkably consistent with those reported recently for the dinuclear 1,3,2,4-diazadiphosphetidine $[(C_6H_5-NH)P_2(NC_6H_5)2]_2NC_6H_5,^{11}$ $[(C_6H_5NH)_2P]_2NC_6H_5,^{5}$ and $[(C_6H_5)2PN(CH_3)P(C_6H_5)NtC_4H_9]_2.^{12}$ Spectral data (¹H and ³¹P NMR) shows conclusively that **1**

in solution is a 1,3,2,4-diazadiphosphetidine, as it is in the solid. The two low-field resonances of the ABX pattern of 1 at δ –109.6 and -106.9 are in the region observed previously for cis-1,3,2,4-diazadiphosphetidines.^{2,12} The higher field resonance at δ -62.0 occurs close to that of $[(C_6H_5NH)_2P]_2NC_6H_5$ (δ -67.8),⁵ supporting strongly the presence of the triaminophosphorus moiety in 1. No evidence is obtained for the presence of other isomeric forms of 1 in solution. Thus, the *cis*-diazadiphosphetidine structural type seems to dominate any tendency of the system to form an isomeric, six-membered ring structure analogous to what has been reported recently for $(C_2H_5NPCl)_3$ and $(CH_3NPX)_3$ (X = Cl, Br).^{13,14} However, since the latter structures are deduced largely from ¹H NMR spectral data, the interesting possibility that they can exist as 1,3,2,4-diazadiphosphetidine structural types must be considered.

Thermolysis of 1 in toluene at temperatures above 80 °C results in the slow conversion of 1 to a mixture of 1 and the previously characterized dimer $[(C_6H_5NH)PNC_6H_5]_2$ (2)¹⁵ according to $2[(C_{k}H_{s}NH)PNC_{s}H_{s}]_{s} \rightleftharpoons 3[(C_{s}H_{s}NH)PNC_{s}H_{s}]_{s} (4)$

$$\frac{1}{1} = \frac{1}{2} = \frac{1}$$

After 3 h at 110 °C, a mixture of 1 and 2 in an approximately 1:10 molar ratio results. This appears to represent the equilibrium position for the trimer-dimer reaction at this temperature. So far, attempts to measure reliably equilibrium constants for the reaction have been frustrated by the slow decomposition of reaction

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⁽¹⁰⁾ All calculations were carried out on the University of Colorado's dual 6400's by using programs contained in or based on Iber's Northwestern University Crystallographic Computing Package, the MULTAN 78 package, and Syntex's data reduction routines. The scattering factors used were for neutral atoms ("International Table for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. 4). A complete description of the crystallographic details and the refinement and solution of structure 1.C2H5OH will be published later.

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materials at temperatures at which the rate of trimer-dimer interconversion is appreciable. Experiments to find species which might catlyze the $1 \rightleftharpoons 2$ interconversion reaction or to discover differently substituted aminophosphine systems in which the equilibrium is more facile are in progress currently.

Compounds 1 and 2, through their relationship as shown in eq 4, represent two members of a novel oligomerization series involving species of the general formula $[(C_6H_5NH)PNC_6H_5]_n$. So far, no evidence for the monomer (n = 1) has been obtained. If the tendency toward formation of 1,3,2,4-diazaphosphetidine rings persists in the series, the series is limited and can exhibit besides the monomer (n = 1), dimer (n = 2), and trimer (n = 3), only tetramer (n = 4) $[(C_6H_5NH)PNC_6H_5]_4$ (3). Species of higher



n cannot exist unless structures which contain bond arrangements other than 1,3,2,4-diazadiphosphetidine rings occur. Intensive study of the conditions under which 3 might be formed and isolated seems warranted.

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Supplementary Material Available: Tables of positional and thermal parameters for nongroup atoms and rigid group atoms (3 pages). Ordering information is given on any current masthead page.

Sceptrin, an Antimicrobial Agent from the Sponge Agelas sceptrum

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During a study of Caribbean sponges, we have examined several sponges of the genus *Agelas*, all of which gave ethanolic extracts having antimicrobial activity, in agreement with previous reports.¹ Prior studies by Minale et al.² resulted in the identification of 4,5-dibromo-2-cyanopyrrole as the antimicrobial constituent of the Mediterranean sponge *Agelas oroides*. *A. oroides* also contained 4,5-dibromopyrrole-2-carboxylic acid,³ the corresponding amide, and oroidin (1).⁴ In this communication, we report the

structural elucidation of sceptrin (2), the major antimicrobial constituent of Agelas sceptrum (Lamarck).



Antimicrobial assays of the crude extracts of six Agelas samples revealed the presence of active compounds in all samples. When the crude extracts were partitioned between ethyl acetate and water, A. sceptrum was distinguished by the strong antimicrobial activity of the aqueous phase. Agelas sceptrum, collected at Glover Reef, Belize, was maintained frozen until required. The lyophilized sponge was extracted sequentially with hexane, dichloromethane, and methanol. The acetone-insoluble portion of the methanolic extract was twice chromatographed on Sephadex LH-20 by using first methanol and then 1:1 methanol/chloroform as eluants to obtain a fraction containing the antimicrobial material. This fraction was chromatographed on a LiChrosorb DIOL column by using 1:1 methanol/chloroform as eluant to obtain oroidin (1, 0.5% dry weight) and sceptrin (2, 2.1% dry weight). Traces of a colored impurity were removed by passing an aqueous solution of sceptrin through Sephadex G-10, after which sceptrin (2) (as the dihydrochloride) was crystallized from water. Sceptrin (2), mp 215–225 °C dec, $[\alpha]_D$ –7.4° (c 1.2, MeOH), had the molecular formula $C_{22}H_{24}Br_2N_{10}O_2 \cdot 2HCl \cdot nH_2O.^5$ The electron impact mass spectrum did not show a molecular ion, but the field desorption mass spectrum contained a triplet at m/z 619, 621, 623 $(C_{22}H_{25}Br_2N_{10}O_2)^+$. The following spectral data indicated that sceptrin (2) was a symmetrical dimer of the 2-debromo derivative of oroidin (1): IR (KBr) 3350, 1680, 1625 cm⁻¹; UV (MeOH) 265 nm (ϵ 20850); ¹H NMR (Me₂SO- d_6) δ 2.29 (br s, 1 H), 3.10 (d, 1 H, J = 8 Hz), 3.42 (br s, 2 H), 6.66 (s, 1H), 6.97 (s, 1 H),6.99 (s, 1 H), 7.33 (br s, 2 H), 8.59 (br t, 1 H, $J \simeq 5$ Hz); ¹³C NMR (D₂O) δ 160.8 (s), 145.7 (s), 123.9 (s), 121.6 (d), 111.6 (d), 108.3 (d), 95.2 (s), 41.6, 40.9, 36.9.

Sceptrin (2) formed small crystals in the monoclinic class, and accurate cell constants determined by a least-squares fit of 15 high angle reflections were a = 19.788 (8) Å, b = 13.337 (4) Å, c =13.725 (7) Å, and $\beta = 122.69$ (2)°. Systematic extinctions (h + k = 2n), a calculated density of 1.63 g/cm³, and the presence of chirality were uniquely accomodated by the space group C2, with four molecules of C₂₂H₂₆Br₂Cl₂N₁₀O₂·3H₂O per unit cell. All unique diffraction maxima with $2\theta \le 100^\circ$ were collected on a computer-controlled four-circle diffractometer using graphite monochromated Cu K α (1.54178 Å) radiation and a variable speed ω -scan technique. Of the 2172 unique reflections surveyed in this fashion, 1697 (78%) were judged observed [$F_0 \ge 3\sigma(F_0)$] after correction for Lorentz, polarization, and background effects.

A phasing model was achieved by standard heavy-atom procedures.⁶ The deconvolution of the Patterson synthesis gave the

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⁽⁴⁾ After some confusion, the structure of oroidin (1) was accepted to be that shown.² An interest in solid-state photodimerization reactions prompted us to carry out a single-crystal X-ray diffraction analysis of oroidin. This study reconfirmed the structure shown and details can be found in the supplementary material.

⁽⁵⁾ The elemental analysis of a sample dried at 110 °C over P_2O_5 required one molecule of water per sceptrin molecule while the X-ray study indicated three water molecules per sceptrin.