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Solution Chemistry of Macrocycles. 5.[1] Synthesis and Ligational Behavior toward Hydrogen and Copper(II) Ions of the Large Polyazacycloalkane 1,4,7,10,13,16,19,22,25-Nonaazacycloheptacosane ([27]aneN$_9$)

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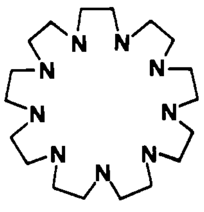
The synthesis and characterization of the new large aza macrocycle 1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane ([27]aneN$_9$) are described. The basicity constants of the macrocycle and the stability constants of the copper(II) complexes were determined by potentiometry at 25 °C in 0.15 mol dm^{-3} NaClO$_4$. The formation enthalpy of the species [Cu$_2$L]$^{4+}$ was determined by batch microcalorimetry. Only binuclear species are formed. The binuclear species [Cu$_2$L]$^{4+}$ is very stable (log k = 36.03), and its formation is exothermic ($\Delta H°$ = −179.1 kJ mol^{-1}). The thermodynamic quantities $\Delta G°$ and $\Delta H°$ as well as the electronic spectral feature of the [Cu$_2$L]$^{4+}$ species indicate that all nitrogen atoms are coordinated to the copper(II) atoms. The macrocycle shows a great tendency to form protonated and hydroxo species: [Cu$_2$LH]$^{5+}$, [Cu$_2$LH$_2$]$^{6+}$, [Cu$_2$LH$_3$]$^{7+}$, and [Cu$_2$LOH]$^{3+}$ are the species present at equilibrium.

Introduction

The adjective "large" has been used to describe polyazacycloalkanes having more than six nitrogen donor atoms.[3] Large polyazacycloalkanes are interesting ligands for the following main reasons: (i) owing to the great number of donor atoms, they can form polynuclear metal complexes in which metal–metal interactions can be studied;[3,4] (ii) these macrocycles are polybases with highly charged protonated species in solution in the neutral pH range. For this reason large polyazacycloalkanes are suitable for "anion-coordination" studies and "supercomplexes" formation.[5,6] The largest polyazacycloalkane so far investigated contained eight nitrogen donor atoms and two copper(II) ions.[3] We have now synthesized the large polyazacycloalkane 1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane containing nine donor atoms ([27]aneN$_9$; hereafter abbreviated as L) and studied its ligational behavior toward hydrogen (basicity) and copper(II) ions.


L

Experimental Section

Ligand Synthesis. All chemicals were reagent grade and were utilized without further purification.

1,4,7,10-Tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazadecane (B). See Figure 1. In a 2-dm^3 three-necked round-bottom flask equipped with mechanical stirrer and condenser, 19 g of 1,4,7,10-tetraazadecane (trien) (0.13 mol) was dissolved in 200 cm^3 of water containing 30 g of NaOH. A solution of 100 g of *p*-tolylsulfonyl chloride (0.53 mol) dissolved in 500 cm^3 of diethyl ether was added dropwise over a period of 6 h, under vigorous stirring. During the addition the reaction mixture was kept at 0 °C and then left at room temperature under stirring overnight. The white crude product formed was filtered off, washed with water, ethanol, and diethyl ether, and then recrystallized from a hot methanol–methylene chloride mixture. The product was dried under vacuum at 50 °C: yield 91 g (92%); mp 219–220 °C; TLC[7] one product with R_f 0.24. Anal. Calcd for C$_{34}$H$_{42}$N$_4$S$_4$O$_8$: C, 53.52; H, 5.55; N, 7.34. Found: C, 53.4; H, 5.4; N, 7.3.

3,6,9,12-Tetrakis(*p*-tolylsulfonyl)-3,6,9,12-tetraazatetradecane-1,14-diol (C). A finely powdered mixture of B (53 g, 0.069 mol), ethylene carbonate (12.16 g, 0.138 mol), and KOH (0.5 g) was placed in a 1-dm^3 three-necked round-bottom flask equipped with mechanical stirrer, condenser, and thermometer. The stirred mixture was heated on an oil bath until it melted and then kept at 170 °C for 4 h. The mixture was allowed to cool at 110 °C, and then 500 cm^3 of methanol was rapidly added. The solution was refluxed for 1 h and then cooled at room temperature with stirring overnight. The product obtained was filtered off, dissolved in 1200 cm^3 of methanol–methylene chloride (10:2), and boiled for 30 min in the presence of activated carbon (2 g). The filtered solution was reduced to 600 cm^3 (cloud point) and allowed to cool slowly. The white crude product obtained was filtered, washed with methanol, recrystallized from hot methanol and a little methylene chloride, and dried in vacuo at 50 °C: yield 32 g (55%); mp 214–216 °C; TLC one product with R_f 0.57. Anal. Calcd for C$_{38}$H$_{50}$N$_4$S$_4$O$_{10}$: C, 53.63; H, 5.92; N, 6.58. Found: C, 53.4; H, 5.8; N, 6.6.

***O*,*O*'-Bis(methylsulfonyl)-3,6,9,12-tetrakis(*p*-tolylsulfonyl)-3,6,9,12-tetraazatetradecane-1,14-diol (D).** A solution of C (34 g, 0.04 mol) and 12.2 g of triethylamine in 500 cm^3 of anhydrous methylene chloride was cooled to −20 °C in a 1-dm^3 four-necked round-bottom flask equipped with mechanical stirrer. To this solution was added dropwise over a period of 20 min, with stirring, a solution of 10.1 g (0.088 mol) of methylsulfonyl chloride in 50 cm^3 of dry methylene chloride. The reaction mixture was kept at −10 °C for 30 min and then was allowed to warm up to room temperature and added to a vigorously stirred mixture of water and ice containing 50 cm^3 of HCl. The organic phase was separated, washed three times with water, and dried over anhydrous Na$_2$SO$_4$. The dry solution was reduced to 100 cm^3 and 500 cm^3 of hot methanol were added. With slow cooling a white powder separated. The crude product was filtered off, washed with methanol and recrystallized from a hot methylene chloride–methanol mixture: yield 28.5 g (70.9%); mp 183–185 °C; TLC one product with R_f 0.31. IR spectra demonstrated that mesilation had occurred since no bands in the O–H region (3000–3500 cm^{-1}) were observed. Anal. Calcd for C$_{40}$H$_{54}$N$_4$S$_6$O$_{14}$: C, 47.84; H, 5.42; N, 5.58. Found: C, 47.7; H, 5.4; N, 5.6.

1,4,7,10,13-Pentakis(*p*-tolylsulfonyl)-1,4,7,10,13-pentaazatridecane (F). The starting material was obtained from the commercial 1,4,7,10,13-pentaazatridecane (E) (Fluka product) by double distillation under reduced pressure. The fraction collected was that between 265–270 °C at 0.1 Torr. A solution of (E) (19.9 g, 0.105 mol) in 100 cm^3 of pyridine was added to a solution of *p*-tolylsulfonyl chloride (100 g, 0.53 mol) placed in a 1-dm^3 four-necked round-bottom flask equipped with mechanical stirrer. The addition of the pentaamine (E) solution was

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[2] (a) University of Florence. (b) University of Valencia.

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[7] TLC measurements were carried out on precoated TLC plates of silica gel 60 F-254 (Merck) with a chloroform–acetone (50:1) mixture as eluent. In the case of product D (see Figure 1), the mixture was 10:1 in the same components.

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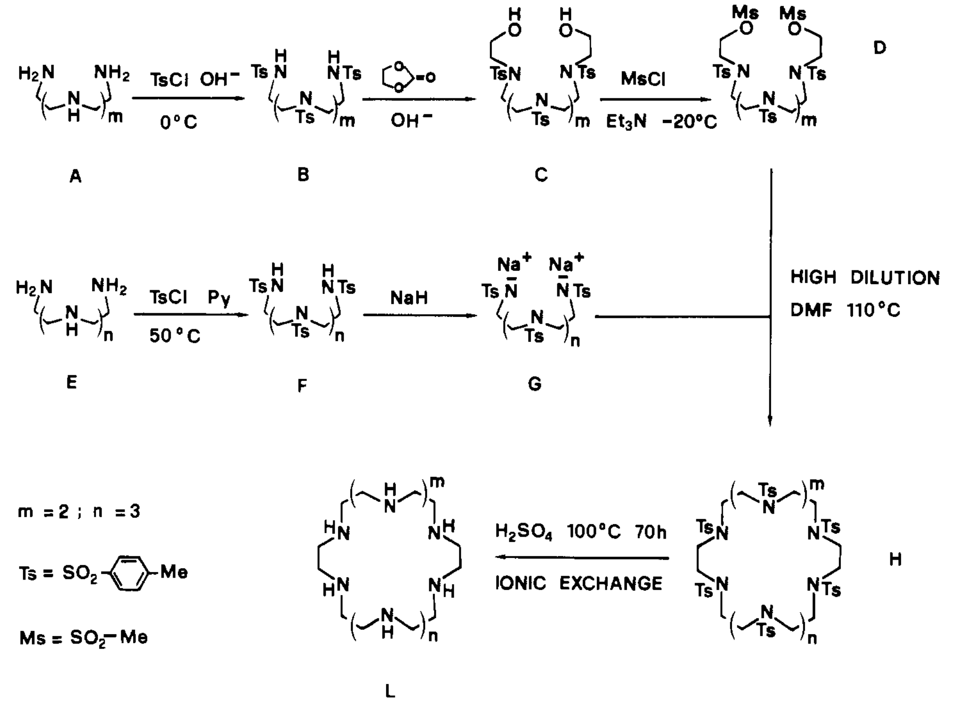

Figure 1. Reaction sequence for the synthesis of the macrocycle (L).

carried out in such a way that the reaction temperature was kept at 40–50 °C. After the addition the reaction mixture was maintained at 50 °C for 2 h and then was allowed to cool at room temperature and added to a vigorously stirred mixture of water and ice (2.5 dm^3), containing the amount of concentrated HCl necessary to neutralize the pyridine. The product obtained was filtered off, washed with water and ethanol, and dissolved in 300 cm^3 of chloroform. The resulting solution was washed with 1 mol dm^{-3} HCl and water three times and dried over Na_2SO_4. To the filtered, warm solution 1 dm^3 of hot ethanol was added. On cooling, a white product separated. The product was filtered off, washed with ethanol and diethyl ether, recrystallized from a chloroform–ethanol mixture (1:4), and dried in vacuo at 50 °C: yield 40.7 g (40.5%); mp 173–175 °C; TLC one product with R_f 0.31. Anal. Calcd for $C_{43}H_{53}N_5S_5O_{10}$: C, 53.76; H, 5.77; N, 7.30; S, 16.70. Found: C, 53.6; H, 5.6; N, 7.2; S, 16.5.

1,4,7,10,13,16,19,22,25-Nonakis(*p*-tolylsulfonyl)-1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane (H). A solution of F (19.2 g, 0.02 mol) in 1 dm^3 of anhydrous DMF was treated with sodium hydride (10 g) in small portions under nitrogen. When hydrogen evolution had ceased, the solution was filtered in one of the two additional funnels of a high dilution device. In the second funnel a solution of D (20.2 g, 0.02 mmol) in 1 dm^3 of anhydrous DMF was placed. The two solutions were added simultaneously and at a constant rate to 0.5 dm^3 of anhydrous DMF vigorously stirred and heated at 110 °C in a 3 dm^3 round-bottom flask. The addition was carried out over 4 h, and then the temperature was maintained at 110 °C for a further hour. The resulting solution was then reduced to 200 cm^3 and then added to a stirred mixture of water and ice (3 dm^3). The crude product obtained was filtered off, washed with water and then ethanol, and dried. Chromatography of the residue over a silica gel (230/400 mesh) column (300 g, 6 cm in diameter) with chloroform gave a solution free of high molecular weight side reaction products. To the concentrated (100 cm^3) eluted solution was added 1 dm^3 of hot ethanol. The white product separated on cooling and was filtered off, dried, and recrystallized from benzene: yield 5.6 g (16%); mp 253–256 °C; TLC one product with R_f 0.69. IR spectra demonstrated that cyclization had occurred since no bands in the N–H region (3060–3500 cm^{-1}) were observed. Anal. Calcd for $C_{81}H_{99}N_9S_9O_{18}$: C, 54.80; H, 5.62; N, 7.10. Found C, 54.6; H, 5.6; N, 7.0.

1,4,7,10,13,16,19,22,25-Nonaazacycloheptacosane (L). A 1.5-g (0.85-mmol) sample of H was dissolved in 15 cm^3 of H_2SO_4 (96%), and the solution was heated at 110 °C on an oil bath for 70 h. A total of 100 cm^3 of cooled (0 °C) ethanol was added in small portions and 100 cm^3 of diethyl ether was then added to the solution, and the white crude product obtained was filtered and washed with ethanol. The dried product was dissolved in water and eluted through an ionic exchange resin (Dowex 1 X8, alkaline form). The solution containing the free amine was distilled to dryness in vacuo. The amine was purified as the nonahydrochloride tetrahydrate; yield 0.57 g (85.6%). Anal. Calcd for $C_{18}H_{62}N_9Cl_9O_4$: C, 27.44; H, 7.93; N, 16.00. Found: C, 27.5; H, 7.9; N, 16.0. The ^{13}C NMR spectrum of L·9HCl (water with 15% D_2O, 20 MHz) consists of only one signal at δ 44.4 (–CH_2–).

Synthesis of Copper(II) Complexes. A boiling solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.1 mmol in 5 cm^3 of absolute ethanol) was added to a boiling solution of L (0.05 mmol in 50 cm^3 of absolute ethanol). The blue precipitate of $Cu_2L(ClO_4)_4{\cdot}H_2O$ immediately formed was filtered and dried in vacuo. (*Caution*! Perchlorate salts of metal complexes can be explosive and must be handled with care. Compounds should not be heated as solids.). Anal. Calcd for $C_{18}H_{47}N_9O_{17}Cu_2Cl_4$: C, 23.23; H, 5.09; N, 13.55. Found: C, 23.1; H, 5.0; N, 13.4%.

Materials. All potentiometric measurements were carried out in 0.15 mol cm^{-3} $NaClO_4$ (C. Erba ACS grade) purified according to the procedure already described.[8] Standardized CO_2-free solutions of NaOH, used in the potentiometric titrations, were prepared by following the procedure described in ref 9.

Emf Measurements. The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, cell, microcomputer, etc.) that has been fully described.[10] One titration curve (81 data points) has been used to determine the basicity constants of L. Two titration curves (115 data points) have been used to obtain the copper(II) complex formation constants. The computer program SUPERQUAD[11] was used to process data and calculate both basicity and stability constants.

Calorimetric Measurements. All calorimetric measurements were performed with an LKB BATCH Model 10700-2 microcalorimeter. The direct reaction between Cu(II) and the macrocycle L is fast; the heat of reaction was measured by mixing an aqueous solution of copper(II) chloride with a solution containing the neutralized appropriate hydrochloric macrocyclic salt. Under the reaction conditions (25 °C, I = 0.15 mol dm^{-3}) and with use of the determined stability constants, the species present and their percentages at equilibrium before and after mixing were calculated by means of the DISPOL[12] computer program. The only significant species present at equilibrium before and after mixing were the free nonprotonated ligand and the complex $[Cu_2L]^{4+}$. Blank experiments were carried out to correct for the enthalpy of dilution of the NaOH solution.

Spectroscopy. Proton-decoupled ^{13}C NMR spectra were recorded with a Varian FT-80A spectrometer operating at 20.0 MHz using water with 15% (w/w) D_2O as solvent; chemical shifts are reported in ppm from $SiMe_4$ with dioxane as secondary reference standard [δ(dioxane) = δ($SiMe_4$) + 67.4]. The electronic spectra were recorded on a Perkin-

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Table I. Thermodynamic Parameters for Basicity and Formation of Cu(II) Complexes with L in Aqueous Solution (25 °C in 0.15 mol dm^{-3} $NaClO_4$)

reaction	log K
$H^a + L = HL$	9.59 (1)^b
$H + HL = H_2L$	9.40 (1)
$H + H_2L = H_3L$	8.77 (1)
$H + H_3L = H_4L$	8.27 (1)
$H + H_4L = H_5L$	6.37 (1)
$H + H_5L = H_6L$	4.22 (1)
$H + H_6L = H_7L$	3.24 (1)
$H + H_7L = H_8L$	2.31 (2)
$H + H_8L = H_9L$	1.8 (1)
$2Cu + L = Cu_2L$	36.03 (4)^{b,c}
$2Cu + L + H = Cu_2LH$	40.66 (4)
$2Cu + L + 2H = Cu_2LH_2$	43.83 (4)
$2Cu + L + 3H = Cu_2LH_3$	47.10 (5)
$Cu_2L + H = Cu_2LH$	4.63
$Cu_2L + 2H = Cu_2LH_2$	7.80
$Cu_2L + 3H = Cu_2LH_3$	11.07
$2Cu + L + H_2O = Cu_2LOH + H$	26.24 (4)
$Cu_2L + OH = Cu_2LOH$	3.94

[a] Charges omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure. [c] $-\Delta G° = 205.6$ (2) kJ mol^{-1}; $-\Delta H° = 179$ (1) kJ mol^{-1}; $T\Delta S° = 26$ (1) kJ mol^{-1}.

Elmer Lambda 9 spectrophotometer.

Results and Discussion

Synthesis of Macrocycle. The synthetic procedure described above for the preparation of the large polyazacycloalkane L was modeled on the general procedure described by Atkins et al.[13] for compounds of this type. Definitive improvements in some of the synthetic steps have been achieved by the use of liquid chromatography for purification and high dilution techniques.

Protonation of Macrocycle. The observed basicity constants for macrocycle L are reported in Table I. The results show that macrocycle L behaves as a relatively strong base in the first protonation steps and as a weaker base in the last protonation steps. This grouping of the basicity constants is typical of azamacrocycles and can be readily explained in terms of charge-repulsion effects.[3,4,14] In the case of large azamacrocycles, the positive charges that accumulate in the macrocyclic framework as the degree of protonation increases experience smaller repulsions than those that accumulate on smaller macrocycles, thus making the difference between the two groups of basicity constants much larger for smaller macrocycles. Macrocycle L behaves as a strong base in the first four protonation steps: the difference between log K_1 and log K_4 is only 1.3 log units (see Table I). Between protonation steps four and five there is a marked difference in basicity (1.9 log units) and this trend continues with the following protonation steps. The last protonation constant is smaller than 2 log units. In order to have relatively accurate values for this basicity constant, corrections for liquid-junction potential (E_j) on the emf readings of the potentiometric curves have been made.[15] It can be seen that in the neutral pH region many highly charged (protonated) species are present, making this large macrocycle suitable for anion coordination studies. Results on the anion-coordination capabilities of this macrocycle will be reported elsewhere.

Copper(II) Complexes. The stability constants for the copper(II) complexes of L are reported in Table I. For the complexes $[Cu_2L]^{4+}$ the thermodynamic parameters ΔH^0 and $T\Delta S^0$ are also reported. Figure 2 shows the distribution diagram for the system Cu(II)–L. The macrocycle L forms very stable binuclear complexes. When the series of polyazacycloalkanes so far investigated is considered, a trend appears for the formation reaction enthalpies of the binuclear species, which are more exothermic as the overall size of the macrocycle increases.[3] In principle two effects can be invoked to explain this trend: (i) increase in the number of donor atoms involved in the coordination to the metal ions; (ii) increase in ligand flexibility and decrease of the electrostatic repulsions between the metal ions coordinated to the larger macrocycle. In the absence of structural details, which in any case would refer to the solid state, we must ask ourselves if all the ligand donor atoms, nine for L, are involved in the coordination to the two copper(II) ions to form the binuclear species $[Cu_2L]^{4+}$. The aqueous solution of the complexes $[Cu_2L]^{4+}$ shows a wide absorption band at 16 500 cm^{-1} ($\epsilon = 220$ dm^3 mol^{-1} cm^{-1}). The following two additional pieces of experimental evidences support the hypothesis that all nitrogen atoms are involved in coordination to the copper(II) ions: (i) the low values of the equilibrium constants for the reaction $[Cu_2L]^{4+} + H^+ = [Cu_2LH]^{5+}$ (see Table I), compared to those for the first protonation of the free macrocycle; (ii) the high exothermicity of the formation reaction for the binuclear species $[Cu_2L]^{4+}$. Furthermore the formation of the complex $[Cu_2L]^{4+}$ is more "exothermic" than that of the related complex $[Cu_2(Bistrien)]^{4+}$ (Bistrien = [24]aneN_8; see ref 3) where eight nitrogen donor atoms are known to be involved in the formation of the binuclear complex. We conclude that for the large macrocycles that we have investigated up to now the ligand flexibility allows all nitrogen donor atoms present in the ligand to be involved in the formation of the binuclear species $[Cu_2L]^{4+}$. In Figure 3 has been reported one of the possible structures of binuclear species in solution. Actually we are synthesizing azacycloalkanes with more than nine donor atoms in order to see if this trend continues and to explore the possibility that more than two metal ions may be inserted into the macrocyclic ring.

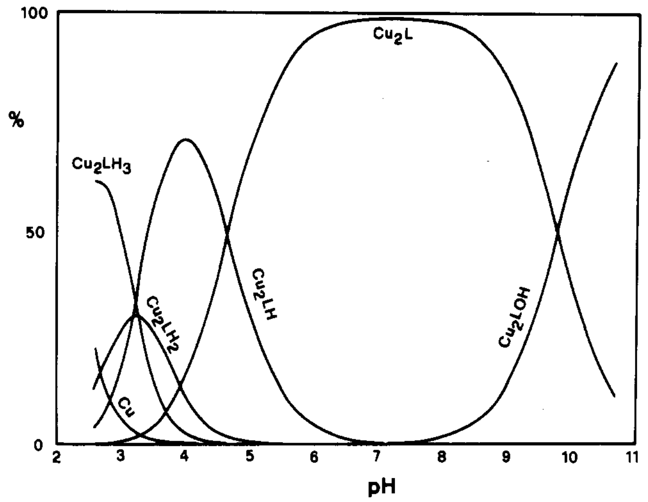

Figure 2. Distribution of species in a solution containing a 2:1 molar ratio of copper(II) to L (charges omitted).

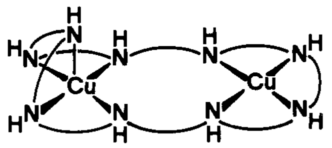

Figure 3. One of the possible structure of the binuclear species $[Cu_2L]^{4+}$.

Due to the abundance of donor atoms available the macrocycle shows some tendency to form polyprotonated dicopper(II) species (see Figure 2). The following species are present at equilibrium: $[Cu_2LH]^{5+}$; $[Cu_2LH_2]^{6+}$; $[Cu_2LH_3]^{7+}$ (see Table I). The poor tendency of the binuclear complex $[Cu_2L]^{4+}$ to protonate itself is shown by the equilibrium constant corresponding to the addition of one proton to the complex (see Table I). This constant is much smaller, for macrocycles L, than that related to the protonation of the first nitrogen in the free macrocycle (see Table I). It is interesting to note that the stepwise protonation constants of the

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binuclear monoprotonated species $[Cu_2LH]^{5+}$ to form more protonated species, $[Cu_2LH_2]^{6+}$ and $[Cu_2LH_3]^{7+}$, 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 $[Cu_2LOH]^{3+}$, 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; $Cu_2L(ClO_4)_4$, 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.

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Synthesis of Two New 1,3,2,4-Diazadiphosphetidine-Based Phosphazane Oligomers: $[(PhNH)P_2(NPh)_2]_2NPh$ and $[(PhNH)PNPh]_3$

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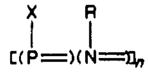
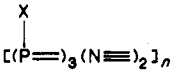
The synthesis of $[(PhNH)P_2(NPh)_2]_2NPh$ (**5**) and $[(PhNH)PNPh]_3$ (**6**), 1,3,2,4-diazadiphosphetidine-based members of new P(III) phosphazane oligomer/polymer series, are reported. **5** is the final product and **6** is an intermediate in the PCl_3–$PhNH_2$ reaction. **5** and **6** have been characterized by spectral (^1H and ^{31}P NMR, IR, and MS) data; **5** has been characterized by single-crystal X-ray crystallography. The monosolvate **5**·CS_2 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)°, $Z = 4$, $d_{calcd} = 1.30$ g/cm³, $d_{obsd} = 1.30$ g/cm³ (24 °C, Mo Kα). **5**·CS_2 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 $(PhNH)_3P$, $[(PhNH)_2P]_2NPh$, $[(PhNH)PNPh]_2$ (**7**), and $[(PhNH)PNPh]_3$ (**6**) enroute to the dinuclear $[(PhNH)P_2(NPh)_2]_2NPh$ (**5**). The mechanisms of phosphazane oligomer formation and interconversion and implications of these for higher phosphazane syntheses are discussed.

Introduction

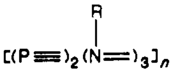
The synthesis and properties of new inorganic macromolecules is of considerable current interest.[2-4] Although a variety of systems are known and being studied actively,[2] glaringly absent are examples of phosphorus(III) polyphosphazanes. These could involve P and N atoms with connectivities to other skeleton atoms of 2:2 (A), 2:3 (B) or 3:2 (C), or 3:3 (D); however, except for phosphorus nitride $(PN)_n$,[3-5] other P(III) polyphosphazanes are not well characterized.


$[(\overset{X}{P}=)(\overset{R}{N}=)]_n$

A


$[(\overset{X}{P}=)_3(N\equiv)_2]_n$

B

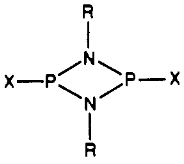

$[(P\equiv)_2(\overset{R}{N}=)_3]_n$

C

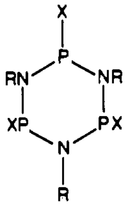
$[(P\equiv)(N\equiv)]_n$

D

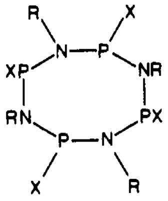
Reactions that might be expected to yield P(III) polyphosphazanes generally yield four-membered-ring 1,3,2,4-diazadiphosphetidines (**1**);[6-8] however with relatively small R groups (R = Me, Et), six- and eight-membered-ring products (**2–4**)[7,9-13] have been obtained. The cyclic phosphazanes (**1–3**) and $(RN)_6P_4$ 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.



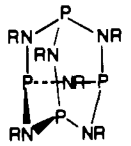
1



2



3



4

$$(R_2PN)_3 \rightleftharpoons (R_2PN)_4 \rightleftharpoons (R_2PN)_n \qquad (1)$$

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 PhN= and P≡ bonding

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