Inorg. Chem. **1984**, *23*, 2550–2552

Table IV. Values of α and β for Copper(II) Complexes

complex	α	β	α/β
$[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$	1.332	0.024	56[d]
$[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$	1.304	0.024	54[d]
$[Cu(tet\ b)(blue)]^{2+}$ [a]	2.189	0.033	66[d]
$[Cu(tet\ a)(blue)]^{2+}$ [a]	1.913	0.031	62[d]
$[Cu(tet\ b)(red)]^{2+}$ [a]	1.512	0.026	57[d]
$[Cu(tet\ a)(red)]^{2+}$ [a]	1.395	0.025	56[d]
$[Cu(2,3,2\text{-}tet)]^{2+}$ [b]	1.440	0.024	60[d]
Cu^{2+} [c]	2.259	0.233	9.7[e]

[a] Reference 2. [b] Reference 4. [c] Reference 13. [d] Soft acid. [e] Borderline acid.

parameters for Cu^{2+} [13] and copper(II) tetraamine complexes.[2,4]

The linear relationship between the values of α and the maxima in the electronic absorption spectra of copper(II) complexes reported in previous papers[2,4] can be extended to these copper(II) macrocyclic complexes, which contain unsaturated nitrogen donors. A plot of α vs. $\bar{\nu}$ gives a strainght line for the copper(II) complexes listed in Table IV. This correlation indicates there appears to be no effect of the macrocyclic ligand other than that which can be described as the equatorial ligand field strength as measured by the energy of the average d–d transition. The values of β for $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$ and $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$ are very similar to those of the planar copper(II) tetraamine complexes, $[Cu(2,3,2\text{-}tet)]^{2+}$, $[Cu(tet\ a)(red)]^{2+}$, and $[Cu(tet\ b)(red)]^{2+}$. The small values of β indicate these complexes are insensitive to the proton basicity of the anionic ligand.

In aqueous solution, copper(II) ion is on the borderline between hard and soft. Addition of two amines and two imines softens the copper(II) and makes it a soft acid, in accord with the symbiosis pointed out by Jørgensen.[14,15] Like copper(II) tetraamine complexes, the softness of $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$ or $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$ is mainly due to the low value of β, insensitivity to the proton basicity factor of the anionic ligand.

On the basis of these results we are able to conclude that the major effect of the macrocyclic ligand is that which can be described as the equatorial ligand field strength as measured by the energy of the average d–d transition.

Acknowledgment. This work was supported by the Chemistry Research Center, National Science Council of the Republic of China, to which the authors express their thanks.

Registry No. $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$, 48186-23-8; $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$, 48186-22-7; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; N_3^-, 14343-69-2; SCN^-, 302-04-5; NO_2^-, 14797-65-0; OAc^-, 71-50-1.

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Syntheses and X-ray Crystal Structures of Two New Classes of Macrocyclic Ligands Having both Phosphorus and Nitrogen Donor Atoms

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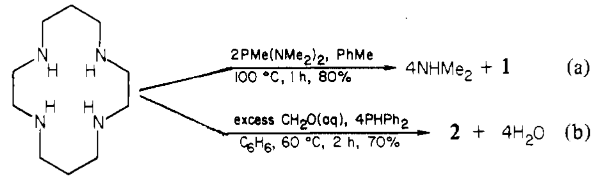
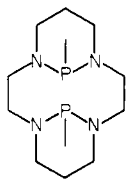
The study of macrocyclic polyhetero ligand systems has attracted much interest, and they have been shown to possess interesting chemical and physical properties.[1,2] However, their syntheses usually involve the use of high-dilution techniques that can, in some cases, limit their availability.[3] In this paper we report one-step high-yield syntheses of two new derivatives of macrocyclic ligands containing phosphorus and nitrogen donor atoms. The syntheses are based upon the derivatization of the cyclam [14]aneN$_4$[4] by simple routes as shown in eq a and b.



cyclam or [14]aneN$_4$
(1,4,8,11-tetraaza-
cyclotetradecane)



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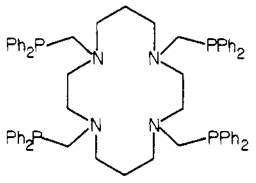

2

Experimental Section

Materials. 1,4,8,11-Tetraazacyclotetradecane[5] and bis(dimethylamino)methyl phosphine, $[P(Me)(NMe_2)_2]$,[6] were synthesized according to literature procedures. Diphenylphosphine (Strem), triethylamine (Aldrich), and formaldehyde (37% aqueous) (Mallinckrodt) were used as purchased. Toluene, hexane, and benzene were dried over Na/K amalgam before use. NMR spectra were obtained by using a Nicolet NT-200 spectrometer operating at 200 or 81 MHz.

$[N_1N_{11},N_4N_8\text{-}(\mu\text{-}PMe)_2[14]aneN_4]$. Bis(dimethylamino)methylphosphine (2.67 g, 20 mmol) in toluene (20 mL) was added to a stirred slurry of 1,4,8,11-tetraazacyclotetradecane (2.00 g, 10 mmol) in toluene (50 mL). After the addition was completed, the mixture was heated at reflux for 3 h, filtered through Celite, and cooled in an acetone/dry ice bath. The product was isolated as a white solid and recrystallized from a 1:2 toluene/hexane mixture. The white crystals were stored under N_2; a second crop was isolated from the filtrate by reducing the volume to 5 mL: yield 2.13 g (74%); mp 157–159 °C; ^1H NMR ($CDCl_3$) δ 1.22 (d, CH_3, $J = 6$ Hz), 2.65 (m, CCH_2C, 4 H), 3.33

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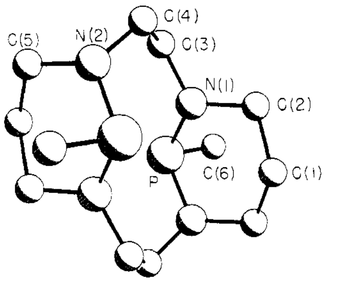

Figure 1. Computer-generated representative diagram for N_1N_{11},N_4N_8-(μ-PMe)$_2$[14]aneN$_4$ (**1**). Important bond distances (Å) and angles (deg): P–N(1) = 1.694 (2), P–C(6) = 1.845 (3), N(1)–C(2) = 1.456 (3), N(1)–C(3) = 1.458 (3), P···P = 4.131 (2), N(1)–P–C(6) = 102.8 (1), C(6)–P–N(2′) = 99.3 (1), N(1)–P–N(2′) = 102.2 (1), P–N(1)–C(2) = 119.2 (1), P–N(1)–C(3) = 120.0 (1), C(2)–N(1)–C(3) = 117.5 (2).

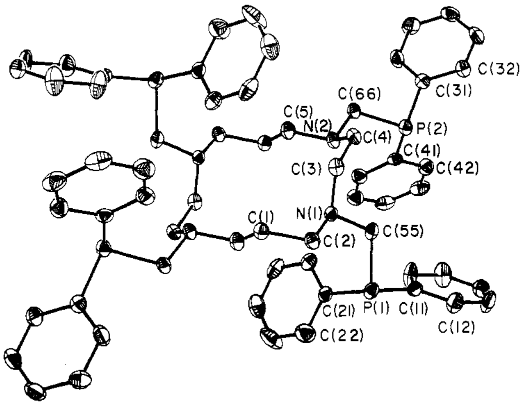

Figure 2. Computer-generated diagram for $(CH_2PPh_2)_4$[14]aneN$_4$ (**2**), showing thermal ellipsoids at the 40% probability level. Important bond distances (Å) and angles (deg): P(1)–C(55) = 1.859 (3), P(1)–C(11) = 1.840 (3), P(1)–C(21) = 1.831 (3), N(1)–C(2) = 1.461 (4), N(1)–C(3) = 1.459 (5), N(1)–C(5) = 1.452 (4), C(11)–P(1)–C(21) = 102.4 (1), C(11)–P(1)–C(55) = 97.1 (1), C(21)–P(1)–C(55) = 102.6 (1), C(2)–N(1)–C(3) = 109.3 (3), C(2)–N(1)–C(55) = 113.9 (2), N(1)–C(55)–P(1) = 115.0 (2), C(3)–N(1)–C(55) = 111.1 (2), P(1)···N(1) = 2.801 (2). Distances and angles at N(2) and P(2) are similar.

(m, NCH_2C, 16 H); ^{31}P NMR ($CDCl_3$) 84.8 ppm.

1,4,8,11-Tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane, $[(N_4C_{10}H_{20})[CH_2P(C_6H_5)_2]_4]$. Diphenylphosphine (2.75 mL, 15.8 mmol) in benzene (25 mL) was added dropwise to a solution containing 1,4,8,11-tetraazacyclotetradecane (0.78 g, 3.9 mmol) and formaldehyde (3.5 mL, 37% aqueous solution) in benzene (50 mL) at 55 °C. After the addition was completed (ca. 15 min), heating was continued for 1 h. The benzene layer was separated from the aqueous layer and dried over anhydrous sodium sulfate. Na_2SO_4 was filtered off and the solvent removed in vacuo. The oily residue remaining was dissolved in a minimum volume of dichloromethane. The product was isolated by the addition of warm ethanol to the solution until a slight cloudiness was produced. Cooling at −20 °C overnight produced the product as colorless, air-stable crystals: yield 2.9 g (74%); mp 139–141 °C; ^{31}P NMR ($CDCl_3$) −27.1 ppm; ^1H NMR ($CDCl_3$) δ 7.36 (m, Ar H, 40 H), 3.34 (m, NCH_2C, 16 H), 2.69 (m, CCH_2C, 4 H), 1.45 (d, CH_2, 8 H, J = 2 Hz).

Structural Determination and Discussion

The structures of **1** and **2** have been determined by single-crystal X-ray diffraction. The crystals of **1** or **2**, selected for data collection, were attached to mounting fibers and placed on the goniometer head in the cold stream of the low-temperature apparatus on a Syntex P2$_1$ diffractometer. The structures were solved by direct methods. All calculations were carried out on a Data General Eclipse computer using the SHELXTL program system. The structures are shown in Figures 1 and 2, crystal data are given in Table I, and atomic coor-

Table I. Summary of Crystal Structure Determinations for Compounds 1 and 2

	1	2
formula	$C_{12}H_{26}N_4P_2$	$C_{62}H_{68}N_4P_4$
fw	288.3	993.16
space group	$P2_1/n$	$P2_1/n$
a, Å	6.519 (3)	14.259 (7)
b, Å	9.488 (8)	9.289 (7)
c, Å	11.730 (6)	20.882 (8)
β, deg	90.71 (4)	104.92 (3)
Z	2	2
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
refinement	least-squares; all atoms isotropic	least-squares; non-hydrogen atoms anisotropic
no. of unique data obsd ($F > 6\sigma(F_o)$)	1426	4897
R	0.043	0.045

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2, ×10^3) for **1**

atom	*x*	*y*	*z*	*U*
P	−1901 (1)	3303 (1)	4645 (1)	14 (1)
C(1)	2180 (3)	2861 (2)	6036 (2)	17 (1)
C(2)	2196 (3)	2766 (2)	4738 (2)	17 (1)
N(1)	543 (3)	3602 (2)	4233 (1)	14 (1)
C(3)	936 (3)	4297 (2)	3148 (2)	16 (1)
C(4)	2381 (3)	5564 (2)	3254 (2)	18 (1)
N(2)	1651 (3)	6773 (2)	3917 (1)	15 (1)
C(5)	−118 (3)	7547 (2)	3446 (2)	18 (1)
C(6)	−2251 (4)	1402 (2)	4341 (2)	21 (1)

Table III. Atom Coordinates (×10^4) and Isotropic Temperature Factors (Å^2, ×10^3) for **2**

atom	*x*	*y*	*z*	U^a
P(1)	3976 (1)	3459 (1)	1832 (1)	25 (1)
P(2)	2302 (1)	694 (1)	−689 (1)	23 (1)
N(1)	5006 (2)	3213 (3)	862 (1)	20 (1)
N(2)	3787 (2)	2688 (3)	−529 (1)	21 (1)
C(1)	6398 (2)	4901 (4)	1080 (2)	23 (1)
C(2)	5859 (3)	3741 (4)	1356 (2)	24 (1)
C(3)	5318 (3)	2291 (4)	390 (2)	23 (1)
C(4)	4515 (3)	1664 (4)	−168 (2)	24 (1)
C(5)	4246 (3)	3822 (4)	−833 (2)	25 (1)
C(11)	2817 (2)	2530 (3)	1775 (1)	24 (1)
C(12)	2823 (3)	1442 (5)	2222 (2)	38 (2)
C(13)	1985 (3)	677 (5)	2207 (2)	44 (2)
C(14)	1135 (3)	1008 (4)	1759 (2)	35 (1)
C(15)	1119 (3)	2074 (5)	1305 (2)	44 (2)
C(16)	1955 (2)	2823 (4)	1312 (2)	41 (1)
C(21)	3577 (2)	5212 (3)	1460 (2)	25 (1)
C(22)	3685 (3)	6364 (5)	1895 (2)	44 (2)
C(23)	3435 (4)	7739 (4)	1671 (2)	57 (2)
C(24)	3060 (3)	7998 (4)	1006 (2)	44 (2)
C(25)	2959 (3)	6869 (4)	571 (2)	33 (1)
C(26)	3223 (2)	5482 (4)	791 (2)	29 (1)
C(31)	1730 (2)	−357 (3)	−1431 (2)	24 (1)
C(32)	1552 (2)	−1810 (3)	−1362 (2)	29 (1)
C(33)	1102 (3)	−2635 (4)	−1905 (2)	34 (1)
C(34)	853 (3)	−2048 (4)	−2526 (2)	38 (1)
C(35)	1029 (3)	−608 (4)	−2605 (2)	42 (1)
C(36)	1455 (3)	227 (4)	−2066 (2)	35 (1)
C(41)	1293 (3)	1881 (4)	−662 (2)	24 (1)
C(42)	440 (3)	1239 (4)	−598 (2)	31 (1)
C(43)	−366 (3)	2051 (4)	−583 (2)	38 (1)
C(44)	−325 (3)	3535 (4)	−615 (2)	37 (1)
C(45)	518 (3)	4178 (4)	−663 (2)	36 (1)
C(46)	1321 (3)	3371 (4)	−685 (2)	30 (1)
C(55)	4305 (2)	2482 (3)	1144 (2)	24 (1)
C(66)	3084 (2)	1877 (3)	−1040 (2)	22 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

dinates and isotropic temperature factors for non-hydrogen atoms are given in Tables II and III.

The structure of **1** is centrosymmetric (imposed) and involves two six-membered PN_2C_3 rings linked at the nitrogens by a pair of $-CH_2CH_2-$ fragments. Alternatively the structure may be described as a puckered, 14-membered cyclam ring in which two $>\ddot{P}Me$ moieties bridge across the 1,11 and 4,8 pairs of nitrogens. The four nitrogens form a plane with projecting $>\ddot{P}Me$ groups on either side. The planarity at nitrogen and the P–N bond distance, 1.694 (2) Å, resemble the geometry of acyclic $>PN<$ compounds.[7] The closest known structures to **1** are the compounds in which a single P,[8] Ti,[9] or V[10] atom has been inserted in the cavity of macrocyclic rings.

Compound **1** is novel in that it contains two extra donor atoms (2 P's) that are 4.131 (2) Å apart. This separation may be compatible (in view of some flexibility in the $-CH_2CH_2-$ link) with P···P distances in trans square-planar (ca. 4.4–4.6 Å) or tetrahedral (3.7–3.9 Å) transition-metal complexes. In view of the high inversion barriers at phosphorus and the constraints of the ring system of **1**, structures in which both P donors bind a metal in a cis fashion are unlikely. Compound **1** may be therefore a member of a rare class[11] of bidentate ligands that should bind trans rather than cis to a metal center. More flexibility could, of course, be introduced by increasing the size of the macrocyclic ring, affording greater movement on the part of the phosphorus atoms and increasing their separation.

The structure of **2**, having a crystallographically imposed center of symmetry, consists of a 14-membered $C_{10}N_4$ backbone with the pairs of $-CH_2PPh_2$ groups on N_1,N_4 and N_8,N_{11} on opposite sides of the cyclam ring. The ligand is therefore potentially an octadentate N_4P_4 ligand with four pairs of bidentate $>PCH_2N<$ units. Ligands of this type have been used extensively to form complexes in which two different transition metals are in close proximity.[12] The bond distances and angles in **2** are normal (see Figure 2 legend), and the P···N separations (2.801 (2) Å for P(1)···N(1)) are close to those found in other $>PCH_2N<$ systems.[12]

The syntheses described for **1** and **2** are likely to be applicable to most macrocycles containing $>\ddot{N}H$ groups and also to primary phosphines. The extension of these methods to allow the isolation of macrocycles with three-dimensional cavities (cavitands) is in progress.

Acknowledgment. We are grateful to the Research Corp. and the NSF (Grant CHE-8116355) for generous financial support and to Dr. Marilyn Olmstead for helpful discussions.

Registry No. 1, 90696-72-3; 2, 90696-71-2; cyclam, 295-37-4; $P(Me)(NMe_2)_2$, 14937-39-4; $PHPh_2$, 829-85-6; CH_2O, 50-00-0.

Supplementary Material Available: Listings of bond distances, bond angles, hydrogen atom coordinates, isotropic and anisotropic temperature factors, and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Stereochemistry of (μ-Sulfato)bis[(*meso*-tetraphenylporphinato)iron(III)]

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Oxyanionic ferric porphyrinates have recently received much attention. The first oxyanionic ligand to be studied was perchlorate.[3] The unusual magnetic properties[3a–c] of these admixed intermediate spin species led in turn to the study of other oxyanionic ligands. Phillippi et al.[4] showed that the nitrato complex, $[Fe(TPP)NO_3]$,[5] was high spin and contained a bidentate nitrato ligand. They also showed that the binuclear sulfato complex $[(Fe(TPP))_2SO_4]$ contains high-spin iron(III) with small or negligible antiferromagnetic coupling between the two iron(III) ions. They suggested on the basis of NMR spectra that the binuclear species had a bridging sulfate ligand in which the sulfate was bound in a bidentate manner. We have investigated the molecular structue of $[(Fe(TPP))_2SO_4]$ and found that the complex contains (in the solid state) a monodentate bridging sulfate ligand.

Experimental Section

Needlelike crystals of $[(Fe(TPP))_2SO_4]$ were obtained by using procedures similar to those reported by Phillippi et al.[4] except that more dilute (1 M) sulfuric acid was used. These crystals diffracted poorly. Recrystallization of these needles from a saturated benzene solution in which *n*-pentane was allowed to diffuse yielded homogeneous crystals of rhombic habit. These crystals did not diffract adequately. Anal. Calcd for $Fe_2SO_4N_8C_{94}H_{62}$: C, 74.71; H, 4.14; N, 7.42. Found: C, 75.12; H, 4.18; N, 7.19. Satisfactory crystals were finally obtained by layering a saturated $CHCl_3$ solution of $[(Fe(TPP))_2SO_4]$ on 50% sulfuric acid and allowing *n*-pentane to diffuse into the two-layered system. Inhomogeneous crystal mixtures were thus obtained. Purple rhombic crystals picked from the mass were found to be adequate for X-ray diffraction studies. Crystals prepared by both methods had characteristic IR spectra in the 800–1000-cm^{-1} region as shown in Figure 1S (supplementary material).

Preliminary examination of a crystal with dimensions of 0.12 × 0.50 × 0.52 mm established a rhombohedral cell with systematic absences consistent with the space groups *R*3*c* or $R\bar{3}c$. Lattice constants (hexagonal setting) ($\bar{\lambda}$ 0.71073) a = 32.431 (7) Å and c = 36.355 (8) Å came from a least-squares refinement that utilized the setting angles of 60 reflections given by the automatic centering routine supplied with the Syntex $P\bar{1}$ diffractometer. These constants gave a calculated density of 1.418 g/cm^3 for a cell content of 18 molecules (including the chloroform and water molecules of crystallization); the experimental density was 1.42 g/cm^3. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C.

Diffracted intensities were measured by θ–2θ scanning with graphite-monochromated Mo Kα radiation. A total of 12836 data to 2θ of 42.93° were measured. Net intensities were reduced as described previously.[6] After they were averaged (merging R factor 0.056), reflections having $F_o > 3\sigma(F_o)$ were taken to be observed. A total of 3499 unique observed data were thus obtained. No absorption

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