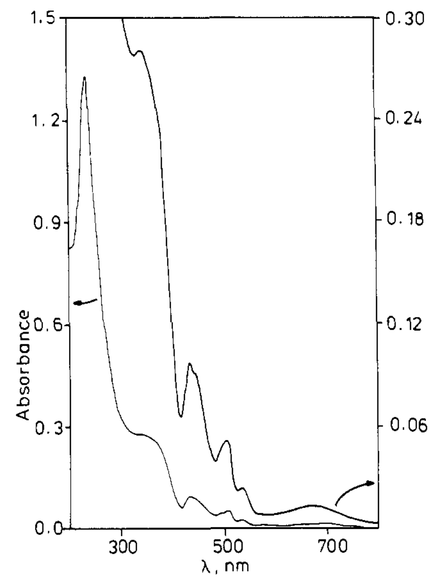

Figure 2. Electronic spectrum of $[L_2Fe_2O(CO_3)_2]\cdot 4.25H_2O$ in acetonitrile ([dimer] = 0.83×10^{-4} M, 1-cm cell).

Figure 2 shows the solution electronic spectrum of $[L_2Fe_2O(CO_3)_2]\cdot 4.25H_2O$ in acetonitrile. Three moderately intense absorption bands in the visible region (990, 677, 536 nm) may be assigned to ligand field transitions of six-coordinate $^6A_1$ ferric ions.[16] The binuclear species then exhibits five intense absorption bands at 506, 445 (sh), 431, 365 (sh), and 340 nm with molar absorption coefficients exceeding 10^3 L mol^{-1} cm^{-1} (except the band at 506 nm), which may be assigned to simultaneous-pair excitation electronic bands and/or Fe–O–Fe charge-transfer bands by following Gray's analysis of the electronic spectrum of $Na_4[(FeEDTA)_2O]\cdot 12H_2O$.[16] The spectrum of $[L_2Fe_2O(CO_3)_2]$ is quite similar to that reported for $[L_2Fe_2O(CH_3CO_2)_2](ClO_4)_2\cdot H_2O$.[12]

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support of this work.

Supplementary Material Available: A full table of crystallographic data (Table S1) and tables containing calculated positional parameters of hydrogen atoms (Table S2), anisotropic thermal parameters of non-hydrogen atoms (Table S3), and intraligand bond distances (Table S4) and angles (Table S5) (5 pages); a table of observed and calculated structure factor amplitudes (Table S6) (12 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of a New Potentially Ditopic Receptor, 1,4,7,10-Tetraoxa-13,16,19,22-tetraazacyclotetracosane, and the X-ray Crystal Structure of Its Mononuclear Copper(II) Complex

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and Vincent Lynch

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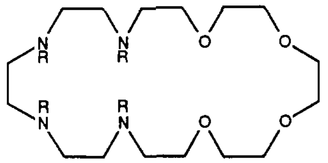
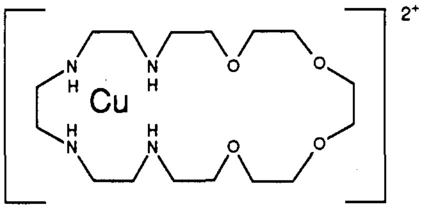
In recent years there has been considerable interest in the development of new macrocyclic binucleating ligands.[1-5] Of particular interest are ditopic receptors containing both hard and soft sites, as these could have a variety of applications in extending the range and scope of coordination chemistry.[6,7] They could, for instance, act to stabilize homodimeric transition-metal complexes in which the two metal centers are in two different oxidation states or perhaps support the formation of heterodimeric metal complexes in which two very different cations (e.g. from group I and the first transition series) are bound within the same macrocyclic framework. In addition, they could act as models for naturally occurring metalloprotein systems.[8-10] Although a number of novel ditopic receptors have now been reported, few of these have relied on using polyaza subunits as one or more of the binding components.[5,11] We therefore sought to develop a crown ether system that would contain, *within the same macrocyclic ligand*, both polyoxa and polyaza subunits as potentially hard and soft binding sites, respectively; we report here the synthesis and characterization of 1,4,7,10-tetraoxa-13,16,19,22-tetraazacyclotetracosane (**2**) and the structure of its 1:1 Cu^{2+} complex **3**.



1 R = Ts

2 R = H



3

Experimental Section

NMR spectra were obtained in $CDCl_3$ with Me_4Si as an internal standard and recorded on a General Electric QE-300 spectrometer. Routine electron impact (EI) mass spectra were measured with a Finnigan MAT 4023 or a Bell and Howell 21-110B instrument. Low-resolution fast atom bombardment mass spectrometry (FAB MS) was performed by using a Finnigan MAT TSQ-70 instrument using 3-nitrobenzyl alcohol as the matrix. Electronic spectra were recorded in methanol on a Beckman DU-7 spectrophotometer. Pentaethylene glycol di-*p*-toluenesulfonate (95% pure) was purchased from Aldrich Chemical Co.

Preparation of 13,16,19,22-Tetratosyl-1,4,7,10-tetraoxa-13,16,19,22-tetraazacyclotetracosane (1). 1,4,7,10-Tetratosyl-1,4,7,10-tetraazadecane[12] (4.74 g, 6.2 mmol) was added to a stirred suspension of 0.35 g of NaH (13 mmol) in 150 mL of DMF. The reaction mixture was stirred and heated at 100 °C under N_2. After 1 h, pentaethylene glycol di-*p*-toluenesulfonate (3.40 g, 6.22 mmol), dissolved in 100 mL of DMF, was added dropwise. The temperature was kept at 100 °C for 20 h. Evap-

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Table I. Crystallographic Data for $Cu(C_{16}H_{36}N_4O_4)(PF_6)_2$

chem formula	$CuC_{16}H_{36}N_4O_4P_2F_{12}$	space group	$P2_1/c$ (No. 14)
		T, °C	−75
a, Å	15.080 (5)	λ(Mo Kα), Å	0.71073
b, Å	20.406 (8)	ρ_{obs}(−75 °C), g/cm^3	1.74
c, Å	8.697 (3)	μ, cm^{-1}	10.47
β, deg	90.16 (3)	transmissn coeff	0.8396–0.9522
V, Å^3	2676 (2)	$R(F)$	0.131
Z	4	$R_w(F)$	0.106
fw	701.96		

oration of the solvent under reduced pressure gave a crude solid, which was dissolved in $CHCl_3$ and washed with 1 N NaOH. The aqueous layer was extracted twice with $CHCl_3$, and the organic layers were combined and dried over $MgSO_4$. The product was purified on silica (3% $CH_3OH/CHCl_3$) and then recrystallized from acetone/H_2O to afford 3.23 g (54%) of **1** as a white crystalline solid: mp 179–185 °C; ^{1}H NMR δ 2.41 (3 H, s, C*H*$_3$Ar–), 2.44 (3 H, s, C*H*$_3$Ar–), 3.31–3.41 (8 H, cluster, –C*H*$_2$N–), 3.44–3.57 (8 H, cluster, –C*H*$_2$O–), 7.29 (4 H, dd, aromatic), 7.71 (4 H, dd, aromatic); ^{13}C NMR δ 21.42, 48.60, 48.76, 48.83, 49.67, 70.33, 70.67, 71.12, 127.27, 127.56, 129.70, 136.25, 136.85, 143.22, 143.35; FAB MS *m/e* (relative intensity) 966 (45), 965 (100), 809 (36).

Preparation of 1,4,7,10-Tetraoxa-13,16,19,22-tetraazacyclotetracosane (2). Compound **1** (3.91 g, 4.04 mmol), anhydrous disodium phosphate (4.96 g), and 2% Na amalgam (96 g) were placed in 40 mL of dry methanol. The mixture was heated at reflux under N_2 for 20 h while stirring rapidly. After the mixture was cooled to room temperature, the resulting slurry was decanted into water and extracted three times with chloroform. The organic layers were combined and dried over $MgSO_4$. The $MgSO_4$ was filtered and the solvent removed in vacuo to yield 1,4,7,10-tetraoxa-13,16,19,22-tetraazacyclotetracosane (**2**) (1.26 g, 88.6% yield) as a colorless oil: ^{1}H NMR δ 1.84 (2 H, br, –N*H*–), 2.60–2.70 (8 H, cluster, –C*H*$_2$N–), 3.46–3.57 (8 H, cluster, –C*H*$_2$O–); ^{13}C NMR δ 48.86, 48.92, 70.28, 70.33, 70.48, 70.63; EI MS *m/e* 349 (MH$^+$).

Preparation of a Copper(II) Complex of 2: $Cu(C_{16}H_{36}N_4O_4)^{2+}$ (3). To a stirred solution of **2** (100 mg, 0.29 mmol) in 40 mL of methanol was added $CuCl_2 \cdot 2H_2O$ (49.0 mg, 0.29 mmol). The solution turned deep blue almost immediately, suggestive of complex formation. Stirring was continued at room temperature for an additional 30 min, at which time $AgPF_6$ (73.3 mg, 0.29 mmol) was added. After a white precipitate was filtered off, presumed to be AgCl, the filtrate was allowed to stand overnight, affording deep blue crystals of the Cu^{2+} complex in virtually quantitative yield: FAB MS *m*/E (relative intensity) 411 (23), 220 (100), 205 (76); UV-vis λ_{max} 578 nm. This complex was characterized further by X-ray crystallography (see below and Figures 1 and 2).

Crystal Structure of $Cu(C_{16}H_{36}N_4O_4)(PF_6)_2$. The data crystal was a deep blue needle of approximate dimensions 0.08 × 0.11 × 0.29 mm, grown by slow evaporation from methanol. Data were collected at −75 °C on a Nicolet R3 diffractometer, equipped with a graphite monochromator and a Nicolet LT-2 low-temperature delivery system (Table I). The positional parameters for the non-hydrogen atoms are listed in Table II. The crystal system is monoclinic, and the space group is $p2_1/c$ (No. 14), as uniquely determined from systematically absent reflections. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures with anisotropic thermal parameters for the Cu, P, F, N, and O atoms. Attempts to refine the C atoms with anisotropic thermal parameters resulted in nonpositive-definite temperature factors for many C atoms. The methylene H atoms were calculated in idealized positions and refined with isotropic thermal parameters riding at $1.2U_{iso}$ of the relevant C atom. No H atoms for the N atoms were included in the refinement. The high values for R and R_w are due to the poor quality of the data crystal, which limited the amount and quality of the data that could be obtained. The structure solution and initial refinement were done by using SHELXTL-PLUS,[13] while the final refinement was done by using SHELX76.[14] The scattering factors for the non-H atoms were taken from Cromer and Mann,[15] with anomalous dispersion corrections taken from Cromer and Liberman,[16] while scattering factors for the H atoms were obtained from Stewart, Davidson, and Simpson;[17] the linear absorption coefficient was calculated from values found in ref. 18. Other computer programs are listed in ref 11 of Gadol and Davis.[19]

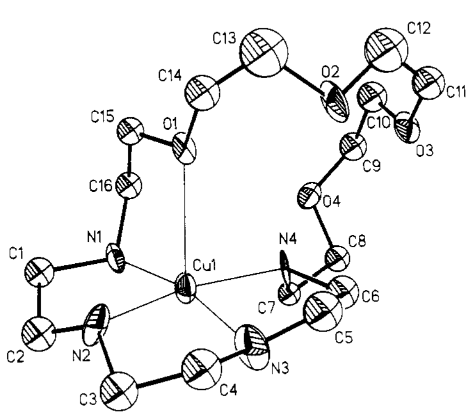

Figure 1. View of $Cu(C_{16}H_{36}N_4O_4)(PF_6)_2$ showing the atom-labeling scheme for the complex and the coordination to Cu. H atoms have been omitted for clarity. Ellipsoids are scaled to the 20% probability level. The Cu^{2+} ion lies 0.10 Å above the plane through the N donors. Relevant Cu bond lengths (Å): 1.98 (2), N1; 1.95 (2), N2; 2.04 (2), N3; 2.05 (2), N4; 2.47 (2), O1. Relevant bond angles (deg): N1–Cu–N2 = 85.8 (9); N1–Cu–N3 = 166.2 (10); N1–Cu–N4 = 106.0 (8); N1–Cu–O1 = 75.8 (7); N2–Cu–N3 = 85.6 (10); N2–Cu–N4 = 167.5 (8); N2–Cu–O1 = 105.9 (8); N3–Cu–N4 = 82.0 (10); N3–Cu–O1 = 117.0 (9); N4–Cu–O1 = 81.3 (7).

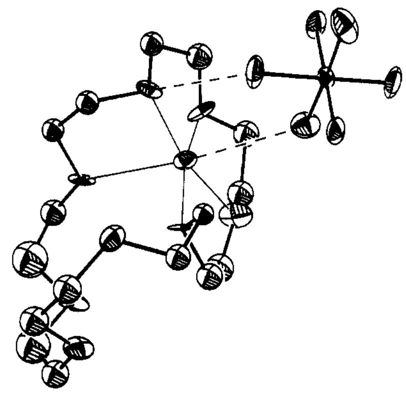

Figure 2. View of cation **3** showing interactions between the central copper atom and one of the PF_6^- counteranions.

Results and Discussion

Ligand Synthesis. The tetratosyl precursor **1** was synthesized by using a method similar to the one developed by Atkins and Richman.[20] The subsequent detosylation of this macrocycle to give the free amine was complicated by the presence of ether functionalities. The ether linkages were prone to cleavage when acidic procedures sufficient to remove tosyl groups (H_2SO_4 at 105 °C for 2 days or 30% HBr/AcOH heated at reflux for 2 days) were used. To avoid this problem, a reductive detosylation involving a 2% Na amalgam was employed.[21] In our hands, this procedure affords a clean and highly efficient method for removing the tosyl groups.

Metal Complex Formation. Solutions of **2** in methanol turned deep blue upon the addition of 1 equiv of cupric chloride. Following exchange of the chloride counterion for hexafluorophosphate, deep blue crystals of the 1:1 copper complex formed upon slow evaporation of the methanol solvent. The structure of this complex was determined by a single-crystal X-ray structural analysis. A labeled diagram of the copper complex is shown in Figure 1 along with relevant bond distances and bond angles.

The geometry of the Cu is a distorted square pyramid with the four nitrogen atoms from the macrocycle occupying the basal positions at a distance of 1.95–2.05 Å and a ligand oxygen atom, O1, 2.47 Å from the copper center occupying the apical position.

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Table II. Fractional Coordinates for Non-Hydrogen Atoms of $Cu(C_{16}H_{36}N_4O_4)(PF_6)_2$

atom	*x*	*y*	*z*
Cu1	0.2457 (3)	0.5995 (14)	0.0299 (4)
N1	0.1352 (14)	0.0770 (10)	−0.087 (2)
N2	0.2833 (15)	0.1466 (12)	−0.040 (2)
N3	0.353 (2)	0.0638 (14)	0.173 (32)
N4	0.2276 (13)	−0.0284 (8)	0.138 (2)
O1	0.2566 (13)	−0.0126 (9)	−0.197 (2)
O2	0.361 (2)	−0.1205 (10)	−0.099 (3)
O3	0.2436 (14)	−0.2025 (9)	0.073 (2)
O4	0.0877 (13)	−0.1258 (10)	0.096 (2)
C1	0.145 (2)	0.1421 (14)	−0.164 (3)
C2	0.207 (2)	0.182 (2)	−0.079 (3)
C3	0.342 (2)	0.171 (2)	0.071 (3)
C4	0.404 (2)	0.116 (2)	0.121 (3)
C5	0.378 (2)	0.003 (2)	0.198 (4)
C6	0.304 (2)	−0.0394 (15)	0.228 (3)
C7	0.144 (2)	−0.0353 (12)	0.220 (3)
C8	0.118 (2)	−0.1028 (13)	0.242 (3)
C9	0.091 (2)	−0.1942 (15)	0.073 (3)
C10	0.169 (2)	−0.217 (2)	−0.010 (3)
C11	0.325 (2)	−0.217 (2)	0.005 (3)
C12	0.354 (3)	−0.191 (2)	−0.113 (5)
C13	0.439 (3)	−0.099 (2)	−0.259 (5)
C14	0.331 (2)	−0.038 (2)	−0.269 (3)
C15	0.180 (2)	0.0017 (13)	−0.285 (3)
C16	0.111 (2)	0.0210 (14)	−0.189 (3)
P1	0.0595 (6)	0.1395 (4)	−0.5603 (7)
P2	0.4504 (8)	0.3610 (4)	0.1085 (8)
F1	0.0651 (11)	0.2029 (7)	−0.7519 (13)
F2	0.0327 (12)	0.0981 (8)	−0.7987 (13)
F3	0.0480 (11)	0.0756 (7)	−0.5516 (13)
F4	0.084 (2)	0.1791 (8)	−0.507 (2)
F5	−0.0392 (13)	0.1545 (8)	−0.624 (2)
F6	0.1572 (10)	0.1226 (8)	−0.688 (2)
F7	0.4539 (13)	0.4039 (7)	0.260 (2)
F8	0.467 (2)	0.4234 (8)	0.011 (2)
F9	0.453 (2)	0.3176 (8)	−0.037 (2)
F10	0.435 (2)	0.3003 (8)	0.208 (2)
F11	0.3505 (15)	0.370 (2)	0.099 (3)
F12	0.5531 (14)	0.3535 (11)	0.122 (2)

This deviation from octahedral coordination by elongation along one 4-fold axis, arising from Jahn–Teller distortion, is typical of Cu^{2+} complexes. Figure 2 includes one of the two hexafluorophosphate counteranions present in the unit cell. This figure shows the presence of a weak interaction between a fluorine atom and the central copper atom. Also of interest is the appearance of an apparent hydrogen-bonding interaction in the same hexafluorophosphate anion and the hydrogen presumably attached to a nitrogen atom on the macrocycle. This H-bonding interaction may exert a stabilizing influence and, thus, play a role in orientating this PF_6 anion in the unit cell.

The d^9 configuration makes Cu(II) subject to Jahn–Teller distortion when placed in an environment of octahedral symmetry.[22] The most common distortion is an elongation along one 4-fold axis, resulting in a plane of four short basallike Cu–L bonds and two long apical-type bonds. Depending on the nature of the ligands, the observed geometry can extend anywhere from a pseudooctahedral structure to a limiting case of square planar. In complex **3** the distorted-square-pyramidal geometry observed about copper (Figure 1) could also be considered as pseudooctahedral (Figure 2), with a hexafluorophosphate anion serving to occupy a position trans to atom O1. The large distance (3.07 Å), however, between this fluorine atom and the central copper leads us to consider that five-coordinate square-pyramidal configuration is a more accurate limiting description of the copper coordination geometry in complex **3**. Such a conclusion seems reasonable in light of a variety of earlier structures obtained with a number of other mono- and dinuclear copper-containing complexes derived from unrelated polyaza crown systems.[5,8,23]

Conclusion

We have established the synthesis and structure of a potentially ditopic receptor. Further, its complex with copper has been elucidated. Studies are currently going on to probe the binding of two metals within this cavity. Initial attempts to bind Na$^+$ to **3**, however, have met with little success: Little or no change was observed in the visible spectrum upon adding Na$^+$ to **3**. Moreover, no change in the FAB MS was observed following this addition. This suggests that the macrocycle **2** may be too small to accommodate the Coulombic repulsion accruing from the binding of two cations within close cocomplexed proximity. In light of recent work showing the binucleating capability of 1,4,7,10,13,16,19,22-octaazacyclotetracosane,[24] we are continuing to investigate the properties of **2** as a ditopic receptor. Indeed, it has been shown by Busch and co-workers[25] that macrocycle size and metal binding ability are interrelated for aza-crowns. With this in mind, a Ni-containing complex has been synthesized.[26] The slightly smaller size of the Ni(II) cation in comparison to that of the Cu(II) cation[27] may allow for a more favorable interaction with a second, putative cobound cation. We are currently exploring this possibility.

Acknowledgment. We are grateful to the National Institutes of Health (Grant No. GM 36384) for financial support of this research.

Supplementary Material Available: Positional and isotropic or equivalent isotropic thermal parameters for the non-H atoms (Table S1), positional and isotropic thermal parameters for the H atoms (Table S2), anisotropic thermal parameters for the Cu, P, F, O, and N atoms (Table S3), bond lengths and angles for the non-H atoms (Table S4), bond lengths and angles for the H atoms (Table S5), and a complete crystallographic summary (Table S6) (16 pages); observed and calculated structure factor amplitudes (Table S7) (22 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of the (*N*,*N'*-Dimethyl-2,11-diaza[3.3](2,6)pyridinophane)copper Dichloride Monohydrate Complex

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and Sebastiano Pappalardo*,§

Received August 17, 1988

The design, synthesis, and ion-binding properties of multiheteromacrocycles, incorporating 2,6-pyridino subunits as part of the macroring, have received much attention in the last decade and remain an active field today.[1] Very little, however, is known about the ligating ability of medium-sized 12-membered [3.3]-

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