2630 *Inorg. Chem.* **1996,** *35,* 2630−2636

Copper(II) Complexes of the Hexaaza Macrocyclic Ligand 3,6,9,16,19,22-Hexaaza-27,28-dioxatricyclo$[22.2.1.1^{11,14}]$octacosa-1(26),11,13,24-tetraene and Their Interaction with Oxalate, Malonate, and Pyrophosphate Anions

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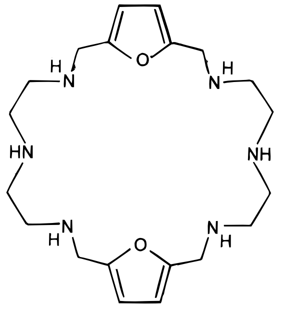
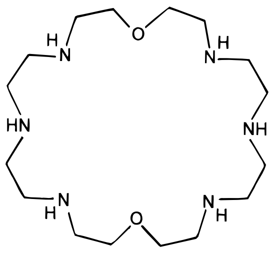
The hexaaza macrocyclic ligand 3,6,9,16,19,22-hexaaza-27,28-dioxatricyclo$[22.2.1.1^{11,14}]$octacosa-1(26),11,13,24-tetraene (BFBD), forms both mono- and dinuclear complexes, as well as several protonated and hydroxo chelates, with Cu(II) ions. These cationic species can bind inorganic and organic anions through coordination and hydrogen bonding. Stability constants of the mono- and dinuclear Cu(II) complexes of BFBD and their interaction with oxalate, malonate, and pyrophosphate anions have been measured potentiometrically. The nature of the bonding between the hosts and the guests is discussed. The crystal structures of two new dinuclear Cu(II) complexes, determined by X-ray crystallography, are also reported. $[BFBDCu_2(Cl)_3]ClO_4\cdot0.5H_2O$ crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 13.267(2)$ Å, $b = 12.155(6)$ Å, $c = 18.461\ 0$ Å, $\beta = 90.86(2)°$, and $Z = 4$. Each Cu(II) ion is coordinated by three nitrogen atoms from the diethylenetriamine unit of the macrocyclic ligand and two chloride anions, forming a square pyramidal geometry. $[BFBDCu_2(Ox)](BF_4)_{1.8}Cl_{0.2}$ crystallizes in the triclinic system, space group $P1$, with $a = 6.772(1)$ Å, $b = 10.646(2)$ Å, $c = 11.517(2)$ Å, $\alpha = 64.74(3)°$, $\beta = 79.79(3)°$, $\gamma = 81.94(3)°$, and $Z = 1$. The environment of each copper is intermediate between square pyramidal and trigonal pyramidal. The oxalate anion bridges in a bis-bidentate fashion between two Cu(II) ions.

Introduction

The chemistry of polyazamacrocyclic ligands is of considerable interest since in addition to complexing cationic species,[1−6] the protonated forms of these ligands and their mononuclear and dinuclear metal complexes can form complexes with anionic substrates.[7−16] In the previous paper,[17] it has been shown that the macrocyclic hexamine ligand 3,6,9,16,19,22-hexaaza-27,28-dioxatricyclo$[22.2.1.1^{11,14}]$-octacosa-1(26),11,13,24-tetraene (BFBD, formula **I**), an analog of the well-known OBISDIEN (formula **II**), is capable of forming mono- through hexaprotonated cationic species which in turn recognize oxalate, malonate, and pyrophosphate anions. The crystal structures of two binary complexes $H_6BFBD{-}C_2O_4^{4+}$ and $H_5BFBD{-}H_2P_2O_7^{3+}$ have confirmed that the binding of anionic substrates to the protonated macrocyclic ligand BFBD is through electrostatic forces and hydrogen bonds.



I, BFBD



II, OBISDIEN

In this paper we report the formation of mono- and dinuclear Cu(II) complexes of BFBD and their interaction with oxalate, malonate, and pyrophosphate anions. Comparisons are made with the corresponding Cu(II) complexes of OBISDIEN. It is noted that BFBD forms less stable mononuclear Cu(II) complexes but is a better dinucleating ligand, probably due to the presence of the two rigid spacers between the two diethylenetriamine units. The crystal structures of two new dinuclear Cu(II) complexes are also reported.

Experimental Section

Materials. Reagent grade $CuCl_2\cdot2H_2O$ was obtained from Matheson Coleman & Bell, GR grade KCl from EM Chemical Co., CO_2-free Dilut-it ampules of KOH from J. T. Baker Inc., and reagent grade oxalic acid from Fisher Scientific Co.

Reagent grade tetrasodium pyrophosphate from Fisher Scientific Co. and malonic acid from Aldrich Chemical Co. were purified by recrystallization from distilled water.

The ligand BFBD was prepared as a colorless crystalline hexahydrochloride by the method previously described.[18]

The Cu(II) solution was standardized by titration with EDTA. The KOH solution was standardized by titration with potassium acid

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⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1996.

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Table 1. Overall Stability Constants for the BFBD−Cu(II) System ($\mu = 0.10$ M (KCl); 25.0 °C): Bf = BFBD, H = H^+, OH = OH^-

stoichiometry					
Bf	Cu	H	log β^a	stepwise quotient K	log K^a
1	1	0	14.70	$[BfCu]/[Bf][Cu]$	14.70
1	1	1	23.21	$[BfCuH]/[BfCu][H]$	8.51
1	1	2	29.93	$[BfCuH_2]/[BfCuH][H]$	6.72
1	1	3	33.32	$[BfCuH_3]/[BfCuH_2][H]$	3.39
1	1	−1	5.28	$[BfCu]/[BfCu(OH)][H]$	9.42
1	2	0	27.30	$[BfCu_2]/[BfCu][Cu]$	12.60
1	2	−1	19.02	$[BfCu]/[BfCu_2(OH)][H]$	8.28
1	2	−2	9.91	$[BfCu_2(OH)]/[BfCu_2(OH)_2][H]$	9.11

[a] Estimated error = ±0.02.

Table 2. Overall Stability Constants and Stepwise Formation Constants for the BFBD−Cu(II)−Ox System ($\mu = 0.10$ M (KCl); 25.0 °C): Bf = BFBD, Ox = Oxalate^{2-}, H = H^+

stoichiometry						
Bf	Cu	Ox	H	log β^a	stepwise quotient K	log K^a
1	1	1	2	34.75	$[BfCuOxH_2]/[BfCuH_2][Ox]$	4.82
1	1	1	3	38.42	$[BfCuOxH_3]/[BfCuH_3][Ox]$	5.10
1	1	1	4	41.92	$[BfCuOxH_4]/[BfCuOxH_3][H]$	3.50
1	2	1	0	33.69	$[BfCu_2Ox]/[BfCu_2][Ox]$	6.39
1	2	1	−1	23.88	$[BfCu_2(OH)Ox]/[BfCu_2(OH)][Ox]$	4.86

[a] Estimated error = ±0.02.

phthalate, and the extent of carbonate accumulation was checked periodically by titration with a standard hydrochloric acid solution.

Potentiometric Measurements. All pH calibrations were performed with standard dilute strong acid at 0.10 M ionic strength in order to measure hydrogen ion concentration directly. Thus p[H] is defined as $-\log [H^+]$

Potentiometric studies of BFBD−Cu(II) systems in the absence and presence of anionic substrates were carried out with a Corning Model 350 pH meter fitted with blue-glass and calomel reference electrodes. Each aqueous system under consideration was measured in a 50 mL jacketed cell thermostated at 25.0 ± 0.05 °C by a refrigerated circulating water bath. The ionic strength was adjusted to 0.10 M by the addition of KCl. The concentrations of the experimental solutions were approximately 2×10^{-3} to 4×10^{-3} M. The stoichiometry of BFBD−Cu(II) systems are 1:1 and 1:2, with a slight (ca. 1%) excess of BFBD. The ternary systems containing BFBD, Cu(II), and anionic substrates were studied at the molar ratios of 1:1:1 and 1:2:1. All systems were studied under anaerobic conditions, established by a stream of prepurified nitrogen. Experimental runs were carried out by adding increments of standard base to a solution containing the acid (hexahydrochloride) form of the macrocycle plus other components. Each p[H] profile was determined by utilizing at least 10 points per protonation equivalent. The range of accurate p[H] measurement was considered to be 2−12. In all potentiometric determinations the σ_{fit},[19] which measures the deviation of the experimental curve and the curve calculated from the equilibrium constants, was less than 0.01 pH unit. A variation in log K of 0.01 to 0.015 was required to produce an observable deviation in the distribution curves. In view of other experimental uncertainties such as the weight of the sample and the volume of the titrant, the error in the constants listed in Tables 1−4 is estimated as ±0.02 log units.

Calculations. Equilibrium constants were calculated with the program BEST.[19] The log K_w for the system, defined in terms of log([H$^+$][OH$^-$]), was found to be −13.78 at the ionic strength employed and was maintained fixed during refinements. In preparation for the quantitative determination of the stability constants of anions with mono- and dinuclear Cu(II) complexes, the protonation constants of the anions and the stability constants of Cu−anion complexes were determined under the conditions of these experiments and are given in Tables S1 and S2. Attempts to potentiometrically determine the stability constants of Cu−pyrophosphate system failed due to the formation of precipitates in solutions containing Cu(II) ion and pyrophosphate anion. The stability constants for the Cu−pyrophosphate system listed in Table S2 are taken from ref 20. Species distribution diagrams were computed from the equilibrium constants with the help of program SPE and plotted with SPEPLOT. Details of the potentiometric method have been described.[19]

Table 3. Overall Stability Constants and Stepwise Formation Constants for the BFBD−Cu(II)−Mal System ($\mu = 0.10$ M (KCl), 25.0 °C): Bf = BFBD, Mal = Malonate^{2-}, H = H^+

stoichiometry						
Bf	Cu	Mal	H	log β^a	stepwise quotient K	log K^a
1	1	1	0	16.97	$[BfCuMal]/BfCu][Mal]$	2.27
1	1	1	1	25.77	$[BfCuMalH]/[BfCuH][Mal]$	2.56
1	1	1	2	33.80	$[BfCuMalH_2]/[BfCuH_2][Mal]$	3.87
1	1	1	3	38.61	$[BfCuMalH_3]/[BfCuH_3][Mal]$	5.29
1	2	1	0	31.54	$[BfCu_2Mal]/[BfCu_2][Mal]$	4.24
1	2	1	−1	22.06	$[BfCu_2(OH)Mal]/[BfCu_2(OH)][Mal]$	3.04

[a] Estimated error = ±0.02.

Table 4. Overall Stability Constants for the BFBD−Cu(II)−Pp System ($\mu = 0.10$ M (KCl), 25.0 °C): Bf = BFBD, Pp = Pyrophosphate^{4-}, H = H^+

stoichiometry						
Bf	Cu	Pp	H	log β^a	stepwise quotient K	log K^a
1	1	1	0	20.68	$[BfCuPp]/[BfCu][Pp]$	5.98
1	1	1	1	29.81	$[BfCuPpH]/[BfCuH][Pp]$	6.60
1	1	1	2	37.28	$[BfCuPpH_2]/[BfCuH_2][Pp]$	7.35
1	1	1	3	43.91	$[BfCuPpH_3]/[BfCuH_3][Pp]$	10.59
1	1	1	4	48.99	$[BfCuPpH_4]/[BfCuH_3][PpH]$	7.12
1	1	1	5	52.62	$[BfCuPpH_5]/[BfCuH_3][PpH_2]$	4.66
1	2	1	0	35.03	$[BfCu_2Pp]/[BfCu_2][Pp]$	7.73
1	2	1	1	41.90	$[BfCu_2PpH]/[BfCu_2][PpH]$	6.05
1	2	1	2	45.36	$[BfCu_2PpH_2]/[BfCu_2][PpH_2]$	3.42
1	2	1	−1	25.76	$[BfCu_2Pp(OH)]/[BfCu_2(OH)][Pp]$	6.74

[a] Estimated error = ±0.02.

Preparation of Crystalline Dinuclear Cu(II) Complexes of BFBD for X-ray Analysis. $[BFBDCu_2(Cl)_3]ClO_4\cdot 0.5H_2O$ (1). A 0.3 mmol sample of BFBD·6HCl and 0.6 mmol of $Cu(ClO_4)_2\cdot 6H_2O$ were dissolved in water and the p[H] of the resulting solution was adjusted to ~7 with 0.1 N NaOH solution. After several days of ethanol diffusion into the solution blue nearly cubic crystals were collected and were suitable for X-ray analysis.

$[BFBDCu_2(Ox)](BF_4)_{1.8}Cl_{0.2}$ (2). A 0.3 mmol sample of BFBD·6HCl, 0.6 mmol of $CuCl_2$ $2H_2O$, 0.3 mmol of $Na_2C_2O_4$, and 3 mmol of $NaBF_4$ were dissolved in water. The p[H] of the resulting solution was adjusted to ~6.5 with 0.1 N NaOH solution followed by slow ethanol diffusion at low temperature. Blue platelike crystals suitable for X-ray analysis were formed after 3 days.

Crystal Structure Determination. A blue nearly cubic crystal of **1** or a blue platelike crystal of **2** was mounted on a glass fiber with epoxy cement. Preliminary examination and data collection were performed with a AFC5R Rigaku single-crystal X-ray diffractometer (oriented graphite monochrometer, Mo Kα $\lambda = 0.710\ 73$ Å radiation) at 163(2) K for **1** and 293(2) K for **2**.[21] Cell parameters were calculated from the least-squares fitting for 25 high-angle reflections. The ω scans for several intense reflections indicated acceptable crystal quality.

Data were collected for $5.04° \leq 2\theta \leq 50.2°$ at 163(2) K for **1** and $4.24° \leq 2\theta \leq 50.10°$ at 293(2) K for **2**. Scan width for data collection was $1.523 + 0.3 \tan(\theta)°$ for **1** and $1.54 + 0.3 \tan(\theta)°$ for **2** in ω with a variable scan rate between 4 and 16° min^{-1}. Weak reflections were rescanned (maximum of two scans) and the counts for each scan were accumulated. Three standards, measured every 150 reflections, showed no significant trends. Background measurement was made by stationary

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crystal and stationary counter technique at the beginning and the end of each scan for half of the total scan time.

Lorentz and polarization corrections were applied to 5217 reflections for **1** and 2752 reflections for **2**. A semiempirical absorption correction was employed.[22] The structure of **1** was solved by direct methods.[23] Full-matrix least-squares anisotropic refinement[24] for all non-hydrogen atoms yielded $R = 0.054$ at convergence. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2.

The structure of **2** was solved by direct methods.[25] Full-matrix least-square anisotropic refinement for Cu(1) and Cu(2) and isotropic refinement for the remaining non-hydrogen atoms yielded $wR(F^2) = 0.184$ and $R(F) = 0.076$ at convergence.[24] Distance constraints were placed on the distorted BF_4 anions and the five-membered ring carbon atoms. Absolute configuration was confirmed by the Flack test.[26] Hydrogen atoms were placed in idealized positions with isotropic thermal parameters riding on the adjacent atoms. Neutral atom scattering factors and anomalous scattering factors were taken from ref 27.

Results and Discussion

Copper(II) Complexes of BFBD. The potentiometric equilibrium curve of the solution containing a 1:1 ratio of Cu(II) ion to BFBD indicates that the initial complex formed contains two protonated nitrogen atoms, which are neutralized at higher p[H]. For the 2:1 ratio of Cu(II) ion to BFBD the potentiometric equilibrium curve shows that all six protons on BFBD are displaced by two Cu(II) ions below p[H] 4.

The equilibrium constants that have been found necessary to explain the potentiometric equilibrium data are presented in Table 1. In addition to the two apparent protonated species of the 1:1 BFBD−copper(II) complex system, $BfCuH^{3+}$ and $BfCuH_2{}^{4+}$, a third less stable protonated form, $BfCuH_3{}^{5+}$, has been found to be necessary to explain the low p[H] data. Also the hydroxo form of the mononuclear Cu(II) complex $BfCu(OH)^+$ is required for a computer fit of the data at higher p[H]. For the 1:2 BFBD−copper(II) system the mono- and dihydroxo dinuclear copper(II) complexes $BfCu_2(OH)^{3+}$ and $BfCu_2(OH)_2{}^{2+}$ are found to be necessary as a result of computer analysis of the equilibrium data.

On the basis of the stability constants in Table 1 the species distribution diagrams (Figures S1 and S2) have been calculated for BFBD−Cu(II) systems (1:1 and 1:2 molar ratios). For the 1:1 system two apparent protonated species, $BfCuH_2{}^{4+}$ and $BfCuH^{3+}$, are the major species in the region of p[H] 4−6 and p[H] 7.2−8.3. The third less stable protonated form, $BfCuH_3{}^{5+}$, only exists in lower concentration below p[H] 5. At p[H] >8 nonprotonated $BfCu^{2+}$ and the monohydroxo form $BfCu(OH)^+$ become the important species in solution. It is also seen that even in the 1:1 system the dinuclear species $BfCu_2{}^{4+}$, $BfCu_2(OH)^{3+}$, and $BfCu_2(OH)_2{}^{2+}$ are also present in solution in considerable concentration from p[H] 3 to p[H] 12, showing that BFBD has a strong tendency to behave as a dinucleating ligand. The species distribution diagram of the 1:2 system is simpler than that of the 1:1 system. The mononuclear protonated species $BfCuH_3{}^{5+}$ and $BfCuH_2{}^{4+}$ exist only at low p[H] as minor species. The dinuclear species $BfCu_2{}^{4+}$ is the predominant complex between p[H] 3.5 and p[H] 8. As the p[H] is further increased, $BfCu_2(OH)^{3+}$ and $BfCu_2(OH)_2{}^{2+}$ form successively due to the hydrolysis of the water molecules which coordinate the Cu(II) centers in $BfCu_2{}^{4+}$.

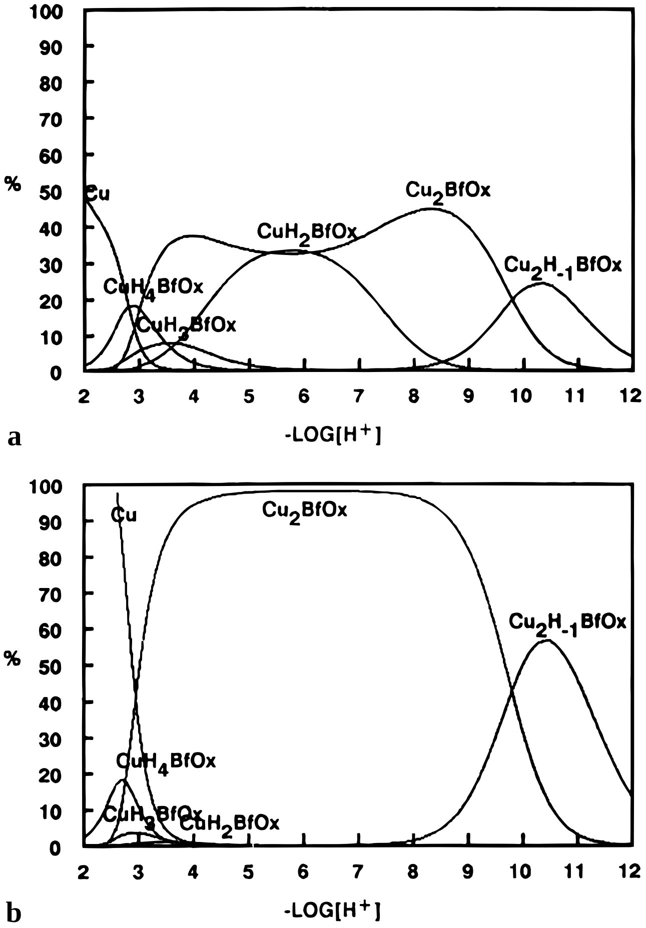

Figure 1. Species distribution diagram showing the species formed as a function of p[H] when (a) 2.00 × 10^{-3} M each BFBD, Cu(II), and oxalate and (b) 2.00 × 10^{-3}M each BFBD and oxalate and 4.00 × 10^{-3} M Cu(II) are equilibrated at 25.0 °C and $\mu = 0.10$ M (KCl). Only the oxalate-containing ternary species are shown.

It is noticed that the stability constant for the mononuclear Cu(II) complex of BFBD, $BfCu^{2+}$ ($\log K_{[BfCu]/[Bf][Cu]} = 14.70$), is relatively lower than that of the corresponding complex of OBISDIEN, $BdCu^{2+}$ ($\log K_{[BdCu]/[Bd][Cu]} = 16.46$).[28] This observation may be interpreted in terms of the different basicities and configurations of these two macrocyclic ligands. From the overall log protonation constants for both ligands ($\log\beta_{H6Bf}{}^{6+} = 39.23$, $\log\beta_{\ H6Bd}{}^{6+} = 41.58$), it is seen that BFBD has lower basicity relative to OBISDIEN and therefore displays weaker coordinate bonding to Cu(II) than does OBISDIEN. Furthermore, BFBD is more rigid due to the presence two aromatic rings, and it is therefore more difficult for the two diethylenetriamine units to coordinate to a single Cu(II) ion. In the case of OBISDIEN, which is quite flexible, the macrocycle can fold to present both diethylenetriamine units for coordination to a single copper(II) ion. The dinuclear Cu(II) complex $BfCu_2{}^{4+}$ ($\log K_{[BfCu2]/[BfCu][Cu]} = 12.60$) on the other hand, is more stable than its analog $BdCu_2{}^{4+}$ ($\log K_{[BdCu2]/[BdCu][Cu]} = 10.79$), with

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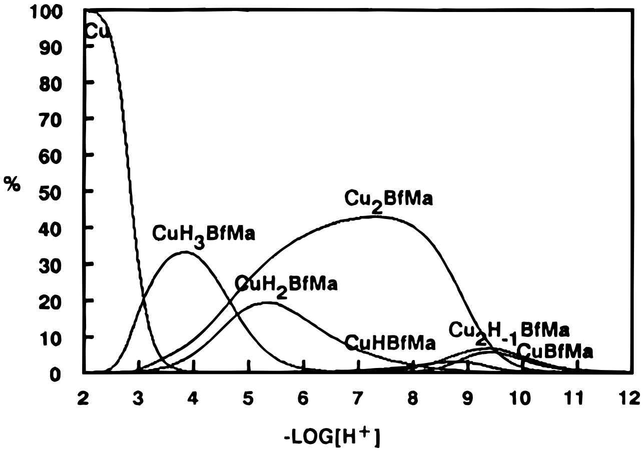
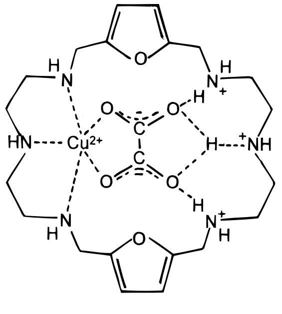


Figure 2. Species distribution diagram showing the species formed as a function of p[H] when 2.00 × 10^{-3} M each BFBD, Cu(II), and malonate are equilibrated at 25.0 °C and μ = 0.10 M (KCl). Only the malonate-containing ternary species are shown.

the stepwise stability constant being almost 2 log units higher. The stronger dinucleating tendency of BFBD is considered to be due to slightly more favorable preorganization of this ligand which provides two diethylenetriamine units at opposite ends of the macrocycle with two rigid furan rings as the bridging groups.

Binding of Oxalate Anion by Cu(II) Complexes of BFBD. The equilibrium constants obtained for the binding of oxalate anion to mono- and dinuclear Cu(II) complexes are presented in Table 2. It is seen that three mononuclear and two dinuclear Cu(II) complexes bind oxalate anion to form ternary complexes, and the dinuclear ternary complex $BfCu_2Ox^{2+}$ is the most stable among these five complexes. For the mononuclear ternary complexes $BfCuOxH_2^{2+}$ and $BfCuOxH_3^{3+}$, the oxalate anion coordinates to the Cu(II) ion at one side of the macrocycle and forms hydrogen bonds with protonated amino groups at the opposite side of the macrocycle. The suggested binding modes of oxalate anion to the mono Cu(II) complex $BfCuH_3^{5+}$ is shown in formula **III**. The mononuclear complex $BfCuOxH_4^{4+}$, however, is an exception in which the oxalate anion may coordinate to a single Cu(II) ion in a chelate fashion instead of being the bridging group between the Cu(II) ion and protonated amino groups. For the dinuclear ternary complexes oxalate anion occupies a bridging position between the two Cu(II) ions which is confirmed by the crystal structure of the dinuclear Cu(II) complex **2** (Figure 4).



III, Possible bonding mode in $BfCuOxH_3^{3+}$

Parts a and b of Figure give the species distribution diagrams of 1:1:1 and 1:2:1 molar ratios of the BFBD−Cu(II)−oxalate systems. It is seen in Figure 1a that even though the stoichiometry favors the formation of mononuclear ternary Cu(II) complexes, none of these mononuclear Cu(II) ternary complexes exceed 35% in concentration, the dinuclear ternary complex $BfCu_2Ox^{2+}$ instead being present over 30% concentration in a wide p[H] range and reaching the maximum of 45% at p[H] 8.3. For the 1:2:1 system the species distribution diagram (Figure 1b) shows that small amounts of mononuclear ternary species exist below p[H] 4, and the dinuclear ternary complex $BfCu_2Ox^{2+}$ is the predominant species from p[H] 3.5 to 9.5. At higher p[H] the hydrolysis of the water molecules coordinated to the Cu(II) centers in $BfCu_2Ox^{2+}$ occurs to form $BfCu_2(OH)Ox^+$ and $BfCu_2(OH)_2Ox$.

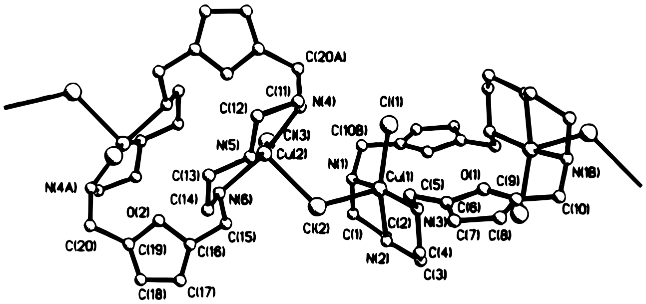


Figure 3. Cation structure and geometry of the dinuclear Cu(II) complex **1** with atomic labeling.

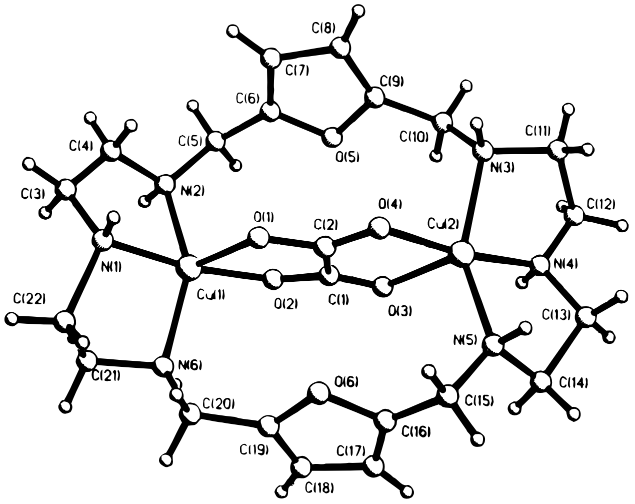


Figure 4. Cation structure and geometry of the dinuclear Cu(II) complex **2**, containing a bridging oxalate anion, with atomic labeling.

Binding of Malonate Anion by Cu(II) Complexes of BFBD. The stability constants listed in Table 3 indicate that both mono- and dinuclear Cu(II) complexes bind malonate anion to form various ternary species, but with lower stability than the corresponding oxalate-containing ternary complexes, in spite of the fact that malonate has more basic donor groups. The lower stability is probably due to the fact that the malonate anion has a methylene group which is considerably hydrophobic and is probably not very well accommodated in this solvated environment. An interesting feature in the 1:1:1 BFBD−Cu(II)−malonate system can be found in the species distribution diagram (Figure 2). None of the mononuclear ternary species, which are favored by the solution composition, exceed 35% in concentration, but the dinuclear ternary species $BfCu_2Ma^{2+}$ remains the major species in the range p[H] 5-9 and reaches its maximum of 43% in concentration at p[H] ≈7.5. This indicates that malonate anion stabilizes the dinuclear complex much more than the mononuclear complex; thus a considerable amount of dinuclear ternary complex Cu_2BfMa^{2+} forms even under unfavorable stoichiometric conditions.

Binding of Pyrophosphate Anion by Cu(II) Complexes of BFBD. The stability constants for the 1:1:1 and 1:2:1 molar ratio of BFBD−Cu(II)−pyrophosphate systems have been determined and are presented in Table 4. The results show that

Table 5. Crystal Data for Dinuclear Cu(II) Complex of BFBD

formula	$C_{20}H_{35}Cl_4Cu_2N_6O_{6.5}$	$C_{22}H_{34}N_6O_6Cu_2B_{1.8}F_{7.2}Cl_{0.2}$
fw	732.42	768.96
space group	*P*21/*n*	*P*1
a, Å	13.267(2)	6.772 (1)
b, Å	12.155(6)	10.646(2)
c, Å	18.461(5)	11.517(2)
α, deg		64.74(3)
β, deg	90.86(2)	79.79(3)
γ, deg		81.94(3)
V, Å^3	2977(2)	737.1(3)
Z	4	1
crystal size, mm	0.28 × 0.24 × 0.2	0.3 × 0.3 × 0.05
limiting indices	$0 \le h \le 15$, $0 \le k \le 14$, $-22 \le l \le +22$	$-8 \le h \le 7$, $-12 \le k \le 0$, $-13 \le l \le +12$
d_{calc}, g/cm^3	1.634	1.732
radiation	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
μ(Mo Kα). mm^{-1}	1.835	1.555
temp, K	163(2)	293(2)
F(000)	1500	389
absolute struct param	0.08 (8)	
R[a]	0.0545	0.0765
wR^2 [b]	0.1392	0.1896

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR = (\sum w(F_o^2 - F_c^2)^2)^{1/2}$. $w^{-1} = \sigma^2F^2 + (x(F_o^2 + 2F_c^2)/3)^2 + y(F_o^2 + 2F_c^2)/3$; $x = 0.085$, $y = 7.64$ for complex **1**, $x = 0.135$, $y = 0.493$ for complex **2**.

there are 10 ternary species formed in the range p[H] 2−12. For the 1:1:1 system the species with the highest stepwise stability constant is $BfCuPpH_3^+$ ($\log K = 10.59$) where the degree of protonation of the mononuclear Cu(II) complex reaches its maximum, while the pyrophosphate anion is completely deprotonated. Therefore both coulombic forces and hydrogen-bonding, which play important roles in host-guest interactions, have been optimized. In the case of 1:2:1 system the species with the highest stepwise stabiliy constant is $BfCu_2$-Pp ($\log K = 7.73$). The affinity of the pyrophosphate anion for $BfCu_2^{4+}$ decreases with increasing protonation of the pyrophosphate anion. It also is noted that the protonation constant of $BfCuPpH_2$ ($\log K = 6.63$) is much higher than that of $BfCuH_2^{4+}$ ($\log K = 3.39$), implying the formation of strong hydrogen-bonding between the substrate and protonated nitrogen atoms.

It is interesting to look at the following equilibria:

$$\mathrm{BfCu^{2+} + Pp^{4-} \rightleftharpoons BfCuPp^{2-}} \qquad \log K_{\mathrm{BfCuPp^{2}}} = 5.98$$

$$\mathrm{BdCu^{2+} + Pp^{4-} \rightleftharpoons BdCuPp^{2-}} \qquad \log K_{\mathrm{BdCuPp^{2}}} = 2.86\,[29]$$

$$\mathrm{BfCu_2^{4+} + Pp^{4-} \rightleftharpoons BfCu_2Pp} \qquad \log K_{\mathrm{BfCu^{2}Pp}} = 7.73$$

$$\mathrm{BdCu_2^{4+} + Pp^{4-} \rightleftharpoons BdCu_2Pp} \qquad \log K_{\mathrm{BdCu^{2}Pp}} = 8.50\,[29]$$

The mononuclear Cu(II) complex $BfCu^{2+}$ is a much better host for the pyrophosphate anion relative to $BdCu^{2+}$, but the dinuclear Cu(II) complex $BfCu_2^{4+}$ is a weaker host than $BdCu_2^{4+}$ toward the same substrate. From the previous discussion it is known that mononuclear Cu(II) complex $BfCu^{2+}$ is less stable than $BdCu^{2+}$; therefore, an additional guest may be more strongly bonded by $BfCu^{2+}$ than $BdCu^{2+}$. In the case of dinuclear Cu(II) complexes, the Cu−Cu separations obtained from the crystal structure for $BfCu_2^{4+}$ and from the MM calculations for $BdCu_2^{4+}$ are 5.34 and 5.39 Å respectively. These suggest that both $BfCu_2^{4+}$ and $BdCu_2^{4+}$ are ideally preorganized to accommodate pyrophosphate anion in a 1,1-Pp mode, but the latter has less steric hindrance due to the lack of two aromatic rings, and therefore binds pyrophosphate anion with higher stability.

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**

	x	*y*	*z*	*U*(eq)[a]
Cu(1)	3237(1)	904(1)	5358(1)	37(1)
Cu(2)	1780(1)	3986(1)	5109(1)	38(1)
Cl(1)	3924(1)	1555(1)	4317(1)	47(1)
Cl(2)	2644(1)	2641(1)	5968(1)	46(1)
Cl(3)	662(1)	2871(1)	4514(1)	50(1)
Cl(4)	648(2)	626(3)	7732(1)	93(1)
O(1)	6721(3)	899(4)	5729(2)	45(1)
O(2)	−1236(3)	4790(4)	6245(2)	44(1)
O(3)	−33(8)	135(16)	7248(7)	391(18)
O(4)	571(7)	142(15)	8434(5)	268(10)
O(5)	1658(5)	460(11)	7514(5)	195(6)
O(6)	452(13)	1776(8)	7805(13)	429(18)
O(7)	3428(27)	2673(14)	7631(9)	249(16)
N(1)	1827(4)	528(5)	4944(3)	43(1)
N(2)	2810(4)	−70(4)	6170(3)	44(1)
N(3)	4604(4)	882(4)	5878(3)	38(1)
N(4)	2892(4)	3959(5)	4345(3)	47(1)
N(5)	2595(4)	5239(4)	5521(3)	44(1)
N(6)	739(4)	4475(4)	5849(3)	37(1)
C(1)	1313(5)	−219(7)	5465(4)	57(2)
C(2)	2081(6)	−868(6)	5892(4)	59(2)
C(3)	3722(5)	−495(6)	6551(4)	53(2)
C(4)	4451(5)	452(6)	6620(4)	50(2)
C(5)	5188(5)	1923(5)	5873(4)	48(2)
C(6)	6260(5)	1747(5)	6087(4)	43(2)
C(7)	6918(5)	2209(6)	6556(4)	51(2)
C(8)	7837(5)	1619(6)	6483(4)	51(2)
C(9)	7690(4)	832(6)	6001(4)	43(2)
C(10)	8261(5)	−177(6)	5822(4)	49(2)
C(11)	3656(5)	4807(7)	4536(5)	68(2)
C(12)	3182(6)	5721(7)	4938(4)	60(2)
C(13)	1923(5)	5969(5)	5926(4)	48(2)
C(14)	1247(5)	5253(6)	6361(4)	48(2)
C(15)	181(5)	3582(5)	6224(4)	44(2)
C(16)	−682(5)	4020(5)	6628(3)	40(1)
C(17)	−1082(5)	3856(5)	7274(3)	40(2)
C(18)	−1950(5)	4553(6)	7300(3)	45(2)
C(19)	−2006(5)	5110(5)	6689(3)	41(2)
C(20)	−2607(6)	6079(6)	6438(4)	55(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

A comparison of the results obtained from the BFBD−Cu(II)−pyrophosphate system with those from the BFBD−Cu(II)−oxalate and the BFBD−Cu(II)−malonate systems shows that the pyrophosphate anion has higher affinity for both mono- and dinuclear Cu(II) complexes. The reason for this behavior are mainly due to two factors. First, completely deprotonated pyrophosphate anion bears a higher charge which makes a greater contribution to the coulombic forces. Second, pyrophosphate anion is much more basic and would be expected to produce stronger Cu−O coordinate bonds.

Crystal Structure of the Dinuclear Cu(II) Complex $[BFBDCu_2Cl_3]ClO_4 \cdot 0.5H_2O$, 1. Figure 3 shows the cationic structure obtained for **1**. A summary of crystallographic results is given in Table 5. Atomic coordinates and selected bond lengths and angles are give in Tables 6 and 7. Each copper(II) ion is five-coordinate, being bonded to three nitrogen donors from a diethylenetriamine unit of the macrocycle and two chloride ions. The geometries around the two copper atoms are almost the same, both being square pyramidal with three nitrogen atoms and one chloride ion forming the basal plane and the other chloride ion at the apical position. The two copper atoms lie 0.2358 and 0.2152 Å above the basal plane and are shifted toward the apical chloride anions. The intramolecular Cu−Cu separation is 5.34 Å.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **1**

Cu(1)−N(2)	1.999(5)	Cu(2)−N(5	2.011(5)
Cu(1)−N(3	2.040(5)	Cu(2)−N(6	2.046(5)
Cu(1)−N(1	2.061(5)	Cu(2)−N(4	2.056(5)
Cu(1)−Cl(1	2.280(2)	Cu(2)−Cl(3	2.278(2)
Cu(1)−Cl(2	2.523(2)	Cu(2)−Cl(2	2.540(2)
N(2)−Cu(1)−N(3)	84.2(2)	N(5)−Cu(2)−N(6)	83.8(2)
N(2)−Cu(1)−N(1)	83.2(2)	N(5)−Cu(2)−N(4)	83.3(2)
N(3)−Cu(1)−N(1)	165.3(2)	N(6)−Cu(2)−N(4)	164.0(2)
N(2)−Cu(1)−Cl(1)	163.4(2)	N(5)−Cu(2)−Cl(3)	167.2(2)
N(3)−Cu(1)−Cl(1)	92.1(2)	N(6)−Cu(2)−Cl(3)	93.1(2)
N(1)−Cu(1)−Cl(1)	97.9(2)	N(4)−Cu(2)−Cl(3)	97.4(2)
N(2)−Cu(1)−Cl(2)	93.9(2)	N(5)−Cu(2)−Cl(2)	90.9(2)
N(3)−Cu(1)−Cl(2)	94.7(2)	N(6)−Cu(2)−Cl(2)	94.2(2)
N(1)−Cu(1)−Cl(2)	93.7(2)	N(4)−Cu(2)−Cl(2)	95.5(2)
Cl(1)−Cu(1)−Cl(2)	102.53(7)	Cl(3)−Cu(2)−Cl(2)	101.67(7)

The macrocycle adopts a chair conformation with the two central nitrogen atoms pointed in opposite directions of the pseudo plane which contains the two furan rings and the remaining four nitrogen atoms. The basal planes of the coordination spheres of the two Cu(II) ions form a dihedral angle of 58.1°. The two furan rings are drawn to each other due to the coordination of two copper atoms by the NNN donor sets of the two diethylenetriamine units, with the two furan oxygen atoms pointing into the macrocyclic cavity. The distance between the two furan oxygen atoms is 5.70 Å, which is much shorter than those in the two previously reported binary complexes of BFBD[17] ($H_6BFBD-C_2O_4^{4+}$ 9.72 Å, $H_5BFBD-H_2P_2O_7^{3+}$ 8.06 Å). It is obvious that this kind of configuration leaves very little space for the dinuclear Cu(II) complex to take up a guest as a bridging group between two Cu(II) ions.

In the crystal the molecules are linked through the chloride ions at the apical position of the copper coordination sites, forming long chains. These chloride anions function as intermolecular bridging groups between the copper atoms from adjacent macrocycles.

Crystal Structure of the Dinuclear Cu(II) Complex $[BFBDCu_2Ox](BF_4)_{1.8}Cl_{0.2}$, 2. Figure 4 illustrates the structure and geometry of the dinuclear cation $[BFBDCu_2Ox]^{2+}$. A summary of crystallographic results, atomic coordinates, and selected bond lengths and angles are given in Tables 5, 8, and 9 respectively. As can be seen, the dinuclear cation consists of two Cu(II) ions which are separated by a bridging group, the bis-bidentate oxalate anion. The Cu−Cu distance is 5.34 Å which is the same as that in the dinuclear Cu(II) complex **1** without any bridging group between the Cu(II) ions. This is not surprising due to the existence of two rigid spacers between two diethylenetriamine units, so that the distance between the two coordination sites is somewhat fixed.

The coordination geometry around each Cu(II) ion can be described as intermediate between the square pyramid and trigonal bipyramid. In the description of the square pyramid, three nitrogen atoms from a diethylenetriamine unit and one oxygen atom from the oxalate anion form the basal plane of the coordination sphere of each Cu(II) ion, with another oxygen atom from the oxalate anion at the apical position. The angles around each Cu(II) ion vary from 80.4 to 98.2° and 80.8 to 98.2°, the $Cu-O_{ap}$ distances being 2.15 and 2.21 Å which are longer than the rest of Cu−N(O) bond lengths. The two Cu(II) ions are displaced by 0.304 and 0.293 Å from the mean basal plane toward the apical oxygen atoms. The trigonal pyramidal structure can be described as two nitrogen atoms from a diethylenetriamine unit and one oxygen atom from the oxalate anion form the equatorial plane of the coordination sphere of each Cu(II) ion with the central nitrogen atom and another oxygen atom from the oxalate anion at axial positions. The pseudotrigonal axes deviate from linearity, N(1)−Cu(1)−O(2) and N(4)−Cu(2)−O(4) being 171.0 and 171.8°.

Table 8. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **2**

	x	*y*	*z*	*U*(eq)[a]
Cu(1)	3255(3)	−4194(3)	10676(2)	34(1)
Cu(2)	−1871(3)	−6968(3)	14813(3)	39(1)
O(1)	3271(34)	−5513(23)	12706(21)	39(6)
O(2)	483(32)	−4629(21)	11092(20)	39(6)
O(3)	−1897(28)	−5538(19)	12750(18)	25(5)
O(4)	1009(24)	−6744(17)	14371(15)	18(4)
O(5)	821(32)	−7861(23)	11983(21)	53(7)
O(6)	650(26)	−3408(19)	13655(18)	36(6)
N(1)	6146(28)	−4062(20)	10320(19)	22(5)
N(2)	4015(54)	−5398(37)	9606(34)	58(10)
N(3)	−1437(50)	−9015(33)	14982(30)	47(9)
N(4)	−4766(34)	−7436(23)	15205(23)	40(7)
N(5)	−2568(40)	−5712(28)	15800(25)	30(7)
N(6)	2809(39)	−2198(27)	10407(24)	29(7)
C(1)	−199(37)	−5293(25)	12305(23)	12(6)
C(2)	1417(56)	−5890(39)	13248(36)	45(10)
C(3)	7043(42)	−4541(29)	9295(27)	38(7)
C(4)	6213(55)	−5602(39)	9563(36)	52(10)
C(5)	2976(68)	−6655(41)	9910(31)	71(14)
C(6)	2671(41)	−7767(35)	11258(25)	48(12)
C(7)	3946(37)	−8739(37)	11954(31)	61(12)
C(8)	2872(39)	−9555(29)	13175(26)	54(10)
C(9)	996(36)	−8998(30)	13137(26)	52(10)
C(10)	−1199(43)	−9188(45)	13756(35)	75(13)
C(11)	−3196(51)	−9712(33)	15892(31)	47(9)
C(12)	−5209(36)	−8688(25)	15555(25)	34(6)
C(13)	−5738(45)	−6931(31)	16161(28)	44(8)
C(14)	−4744(50)	−5419(35)	15950(33)	45(9)
C(15)	−1482(44)	−4535(27)	15637(22)	30(7)
C(16)	−1304(37)	−3453(31)	14282(22)	41(10)
C(17)	−2403(34)	−2403(31)	13511(26)	45(10)
C(18)	−1155(37)	−1672(28)	12343(25)	52(9)
C(19)	676(32)	−2265(25)	12466(21)	38(8)
C(20)	2524(33)	−1815(33)	11521(26)	39(8)
C(21)	4628(52)	−1652(34)	9497(31)	48(9)
C(22)	6318(48)	−2385(35)	10121(35)	61(10)
B(1)	−600(39)	1405(28)	8454(26)	308(82)
F(1)	649(41)	604(29)	9289(25)	157(14)
F(2)	−192(36)	1204(24)	7376(19)	106(7)
F(3)	−2507(34)	1163(32)	8952(31)	156(15)
F(4)	−307(41)	2720(21)	8142(27)	103(12)
B(2)	2108(20)	−2505(14)	6866(14)	18(4)
F(5)	452(44)	−1689(36)	6575(41)	122(21)
F(5′)	1486(54)	−2807(38)	6018(34)	161(19)
F(6)	2834(66)	−2408(41)	7813(32)	136(23)
F(6′)	1752(39)	−1113(20)	6529(26)	84(10)
F(7)	3496(49)	−2225(36)	5837(30)	95(14)
F(7′)	4149(26)	−2727(29)	6804(28)	75(10)
F(8)	1629(47)	−3830(22)	7272(31)	40(11)
F(8′)	1335(55)	−3196(37)	8052(25)	207(26)
Cl(1′)	−1172(76)	1312(52)	10128(48)	64(18)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The macrocyclic ligand adopts a conformation with two furan oxygen atoms pointing outward from the macrocyclic cavity, which allows the oxalate anion to occupy the bridging position between the two Cu(II) ions. The oxalate plane and two furan rings are almost parallel and the steric effects between them are minimized. There is distortion of the coordination geometries of Cu(II) ions in complex **2** from the idealized square pyramid, as in complex **1**, toward the trigonal bipyramid. This reflects the restraints placed upon the molecule by the oxalate bridge and the rigidity of the macrocyclic backbone. The oxalate anion deviates from the planarity with atom-to-plane distances varying from 0.044 to 0.12 Å, Cu(1) being 0.03 Å off the plane and Cu(2) lying in the plane.

Conclusions. BFBD forms both mono- and dinuclear complexes with Cu(II) ions and shows a strong dinucleating

Table 9. Selected Bond Lengths (Å) and Angles (deg) for **2**

Cu(1)−Cu(2)	5.337(3)	Cu(2)−O(4)	1.95(2)
Cu(1)−O(2)	1.92(2)	Cu(2)−N(4)	2.02(2)
Cu(1)−N(1)	1.94(2)	Cu(2)−N(5)	2.06(3)
Cu(1)−N(6)	2.00(3)	Cu(2)−N(3)	2.09(3)
Cu(1)−N(2)	2.09(3)	Cu(2)−O(3)	2.21(2)
Cu(1)−O(1)	2.15(2)		
O(2)−Cu(1)−N(1)	171.0(8)	O(4)−Cu(2)−N(4)	171.8(7)
O(2)−Cu(1)−N(6)	98.0(10)	O(4)−Cu(2)−N(5)	98.2(9)
N(1)−Cu(1)−N(6)	91.0(9)	N(4)−Cu(2)−N(5)	89.7(10)
O(2)−Cu(1)−N(2)	93.2(11)	O(4)−Cu(2)−N(3)	91.4(10)
N(1)−Cu(1)−N(2)	80.4(11)	N(4)−Cu(2)−N(3)	80.8(11)
N(6)−Cu(1)−N(2)	140.0(12)	N(5)−Cu(2)−N(3)	145.5(11)
O(2)−Cu(1)−O(1)	81.8(9)	O(4)−Cu(2)−O(3)	82.5(7)
N(1)−Cu(1)−O(1)	94.4(8)	N(4)−Cu(2)−O(3)	97.6(8)
N(6)−Cu(1)−O(1)	109.9(9)	N(5)−Cu(2)−O(3)	105.1(9)
N(2)−Cu(1)−O(1)	109.6(12)	N(3)−Cu(2)−O(3)	109.0(10)

tendency due to the presence of two coordination sites which are separated by two rigid spacer groups. These Cu(II) complexes in turn bind oxalate, malonate, and pyrophosphate anions with different stabilities. The increase of binding strength with the charge of both hosts and guests, as well as with the basicity of donor groups of the guests, indicates that the strength of the coordinate bonds, electrostatic attractive forces, and hydrogen bonds in the case of protonated mononuclear Cu(II) complexes all contribute to the stabilities of the ternary Cu(II) complexes. The binding of malonate anion by Cu(II) complexes, however, is weaker than that of oxalate anion even though the former has more basic donors. The fact that the malonate anion has a hydrophobic methylene group may partially account for the weaker bonding of this anion by Cu(II) complexes. Furthermore the crystal structure results shows that the distance between the two well-separated coordination sites is mainly determined by the two furan rings, but the orientations of these two spacer groups vary from one complex to another in order to accommodate the bridging groups between the two Cu(II) centers. Thus while the dinuclear Cu(II) complex favors a particular size of bridging group due to a favored Cu−Cu distance, favoring oxalate over malonate binding, the dinuclear macrocyclic complex can contort to bind less than optimally size bridging groups, such as the malonate anion, albeit with greater steric strain. Therefore the distance between the coordination sites in BFBD enables the $BfCu_2^{4+}$ complex to be somewhat preorganized to selectively bind certain sizes of anions as bridging groups.

Acknowledgment. This research was supported by the Office of Naval Research.

Supporting Information Available: Figures S1 and S2, showing distribution curves of macrocyclic Cu(II) complexes and tables of the protonation constants of anions and the stability constants of the Cu(II)−anion complex, bond lengths and angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters (12 pages). Ordering information is given on any current masthead page.

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