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12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Three diaza-18-crown-6 ligands substituted with two each of 5-amino-2-hydroxybenzyl (1), 3-amino-5-chloro-2-hydroxybenzyl (2), or 3-amino-2-hydroxy-5-methylbenzyl (3) units (see Figure 1) were prepared as reported in our Technical Report No. 2 of August 13, 1998. Interaction of the ligands with Na <sup>+</sup> , K <sup>+</sup> , Ag <sup>+</sup> , and Cu <sup>2+</sup> was evaluated by a calorimetric titration technique and the results are shown in Table 1. Heterobinuclear complexes were observed for complexes 2-Cu <sup>2+</sup> -Na <sup>+</sup> and 3-Cu <sup>2+</sup> -Na <sup>+</sup> with log K values of 1.86 and 1.41, respectively (see Table 1). These binuclear complexes are possible since the Cu <sup>2+</sup> ion can interact with the neighboring amino and hydroxy groups of the two appended benzene rings leaving the macrocyclic cavity free for Na <sup>+</sup> . As expected, Cu <sup>2+</sup> -1, with the amino and hydroxy groups <i>para</i> to each other which does not allow a stable coordination array for Cu <sup>2+</sup> , did not form a binuclear complex with Na <sup>+</sup> . Possible structures for 2-Cu <sup>2+</sup> -Na <sup>+</sup> , 3-Cu <sup>2+</sup> -Na <sup>+</sup> , and 1-Cu <sup>2+</sup> are shown in Figure 1.				
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Technical Report No. 3

**Diaza-18-Crown-6 Ligands Containing Two Aminophenol Sidearms: New  
Heterobinuclear Metal Ion Receptors**

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**Table 1.** Log  $K$ ,  $\Delta H$  (kJ/mol), and  $T\Delta S$  (kJ/mol) Values for Interactions of Macrocyclic Ligands with Metal Ions in Methanol Solution at 25.0°C

ligand	cation	log $K$	$\Delta H$	$T\Delta S$
1	Na <sup>+</sup>	2.73 ± 0.06	-24.6 ± 0.7	-9.01
	K <sup>+</sup>	2.81 ± 0.02	-34.8 ± 0.4	-18.8
	Cu <sup>2+</sup>	> 5.5	-65 ± 3	> -33.6
2	Na <sup>+</sup>	3.42 ± 0.04	-12.4 ± 0.7	7.12
	K <sup>+</sup>	a		
	Ag <sup>+</sup>	> 5.5	-47.9 ± 0.5	> -16.5
	Cu <sup>2+</sup>	> 5.5	-68 ± 3	> -36.7
3	Na <sup>+</sup>	3.00 ± 0.05	-7.9 ± 0.8	9.22
	K <sup>+</sup>	2.36 ± 0.08	-10.6 ± 0.7	2.87
	Cu <sup>2+</sup>	> 5.5	-69 ± 3	> -37.6
Cu <sup>2+</sup> -1	Na <sup>+</sup>	a		
Cu <sup>2+</sup> -2	Na <sup>+</sup>	1.86 ± 0.06	8.9 ± 0.4	19.5
Cu <sup>2+</sup> -3 <sup>b</sup>	Na <sup>+</sup>	1.41 ± 0.05	17.8 ± 0.6	25.8

<sup>a</sup>No measurable heat other than heat of dilution indicating that  $\Delta H$  or/and log  $K$  is small.

<sup>b</sup>MeOH solutions of Cu<sup>2+</sup>-ligand (1:1) were titrated by a Na<sup>+</sup>-MeOH solution.

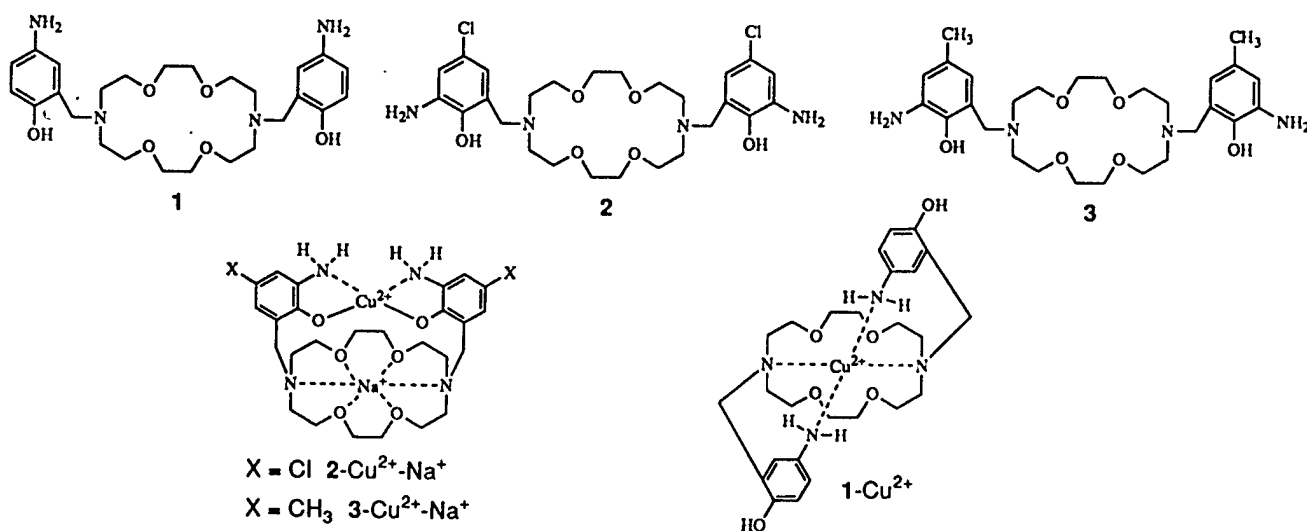


Figure 1.