Articles

Calixresorcinarenes as Ligands: Synthesis and Characterization of Transition-Metal Cavitand Complexes

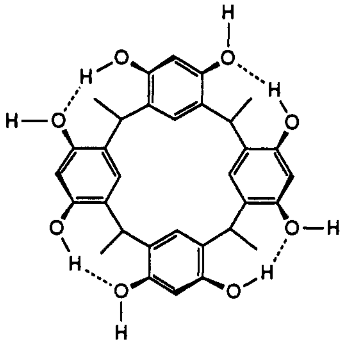
Thomas N. Sorrell,* F. Christopher Pigge, and Peter S. White

Department of Chemistry, The University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27599-3290

Received November 24, 1993[⊗]

A partially-unlinked cavitand, derived from the condensation of acetaldehyde and resorcinol and having three ethylene bridges, functions as a monodentate ligand toward transition metal ions. Treatment of the cavitand with MCl_2 and a bidentate ligand (L) in the presence of NaOH led to isolation of metal complexes with the formula $(cavitand)_2ML$ (M = Co, Cu, Zn) or $(cavitand)_2ML_2$ (M = Ni). The square-planar complexes of Cu(II) and Co(II), the tetrahedral complex of Zn(II), and the octahedral complex of Ni(II) were characterized spectroscopically and in one case by X-ray crystallography. Crystals of Cu(II) complex **4** ($C_{116}H_{133}Br_8CuN_{11}O_{18}$) belong to the triclinic space group $P\bar{1}$ with $a = 13.854(3)$ Å, $b = 21.602(5)$ Å, $c = 22.743(6)$ Å, $\alpha = 110.091(21)°$, $\beta = 98.540(22)°$, $\gamma = 103.922(21)°$, $V = 6002(3)$ Å^3, and $Z = 2$.

The calix[*n*]arenes, derived from the condensation of phenols with formaldehyde, and the related calixresorcinarenes (e.g. **1**), derived from the condensation of resorcinol with aldehydes, are unique bowl-shaped macrocyclic compounds which have found extensive applications in the field of molecular recognition and host–guest chemistry.[1] Potentially, such compounds also might be used in the binding and recognition of transition metal ions, but that topic is largely unexplored.



1

It occurred to us that positioning a metal ion directly in the calixresorcinarene framework, coupled with the inherent ability of these macrocycles to complex small organic molecules, could lead to the development of new and selective catalysts and enzyme mimics. There are several reports demonstrating the ability of the calix[*n*]arenes to form complexes with actinides and lanthanides,[2] main group elements,[3] and transition metals.[4] In contrast, there are no reports of calixresorcinarene complexes with transition metal ions and few involving main group elements.[5] There are also several examples of calixresorcinarenes derivatized with ferrocene moieties along both the upper and lower rims.[6] In no case, however, was the calixresorcinarene framework directly used as a metal-ligating group.

As part of a larger program aimed at the functionalization of the upper rim of rigid calixresorcinarenes (cavitands),[7] we considered the possibility of using the free phenolic residues of the partially-unlinked cavitand **2**[8] as a metal ion ligating moiety. We report here the synthesis and characterization of the first transition metal cavitand complexes.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1994.

(1) (a) Gutsche, C. D. In *Calixarenes, Monograph in Supramolecular Chemistry;* Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1989; Vol. 1. (b) *Calixarenes: A Versatile Class of Macrocyclic Compounds;* Vicens, J., Böhmer, V., Eds.; Kluwer Academic; Dordrecht, The Netherlands, 1991.

(2) (a) Harrowfield, J. M.; Ogden, M. I.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1991**, 979–985. (b) Harrowfield, J. M.; Ogden, M. I.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1991**, 2153–2160. (c) Furphy, B. M.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H.; Wilner, F. R. *J. Chem. Soc., Dalton Trans.* **1989**, 2217–2221. (d) Harrowfield, J. M.; Ogden, M. I.; White, A. H.; Wilner, F. R. *Aust. J. Chem.* **1989**, *42*, 949–958. (e) Engelhardt, L. M.; Furphy, B. M.; Harrowfield, J. M.; Kepert, D. L.; White, A. H.; Wilner, F. R. *Aust. J. Chem.* **1988**, *41*, 1465–1476. (f) Shinkai, S.; Koreishi, H.; Ueda, K.; Arimura, T.; Manabe, O. *J. Am. Chem. Soc.* **1987**, *109*, 6371–6376. (g) Furphy, B. M.; Harrowfield, J. M.; Kepert, D. L.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Inorg. Chem.* **1987**, *26*, 4231–4236.

(3) (a) Delaigue, X.; Hosseini, M. W.; Cian, A. D.; Fischer, J.; Leize, E.; Kieffer, S.; Dorsselaer, A. V. *Tetrahedron Lett.* **1993**, *34*, 3285–3288. (b) Atwood, J. L.; Bott, S. G.; Jones, C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1349–1351. (c) Harrowfield, J. M.; Ogden, M. I.; Richmond, W. R.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1159–1161. (d) Izatt, S. R.; Hawkins, R. T.; Christensen, J. J.; Izatt, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 63–66.

(4) (a) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 1159–1160. (b) Atwood, J. L.; Orr, G. W.; Means, N. C.; Hamada, F.; Zhang, H.; Bott, S. G.; Robinson, K. D. *Inorg. Chem.* **1992**, *31*, 603–606. (c) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 4465–4468. (d) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 1083–1084. (e) Hofmeister, G. E.; Alvarado, E.; Leary, J. A.; Yoon, D. I.; Pedersen, S. F. *J. Am. Chem. Soc.* **1990**, *112*, 8843–8851. (f) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 640–641. (g) Hofmeister, G. E.; Hahn, F. E.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *11*, 2318–2319. (h) Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1986**, 610–611. (i) Olmstead, M. M.; Sigel, G.; Hope, H.; Xu, X.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 8087–8091.

(5) (a) Xu, W.; Vittal, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 6456–6457. (b) Xu, W.; Rourke, J. P.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1993**, 145–147. (c) Cram, D. J.; Stewart, K. D.; Goldberg, I.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2574–2575.

(6) (a) Beer, P. D.; Tite, E. L.; Drew, M. G. B.; Ibbotson, A. *J. Chem. Soc., Dalton Trans.* **1990**, 2543–2550. (b) Beer, P. D.; Tite, E. L.; Ibbotson, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1874–1876.

0020-1669/94/1333-0632$04.50/0

Experimental Section

All reagents and solvents are commercially available and were used without purification. Partially-linked cavitand **2** was prepared according to the procedure of Cram.[8] UV–visible spectra were recorded on a Perkin-Elmer Lambda 6 UV spectrophotometer. EPR spectra were recorded on a Varian E-3 EPR spectrometer. Magnetic susceptibility measurements were obtained on a Guoy balance and were corrected using Pascal's constants.[9] ^{1}H-NMR spectra were recorded on a Bruker AC-200 (200 MHz) spectrometer. Chemical shifts (δ) are reported in ppm downfield from TMS. Elemental analyses were obtained from Atlantic Microlabs, Norcross, GA. Melting points were determined using a Fisher–Johns melting point apparatus and are uncorrected.

General Procedure for the Preparation of Metal Complexes 4–6. The partially linked cavitand **2** was treated with 1.0 equiv of NaOH in MeOH[10] followed by addition of a methanolic solution containing 0.5 equiv of MCl_2 (M = Co, Cu, Ni, Zn) and 0.5 equiv of a bidentate ligand, 1,1-bis(1-methylimidazol-2-yl)-1-methoxyethane (bime) or 4,4′-dimethylbipyridine (Me_2bpy). After several hours of stirring at room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2, and the mixture was filtered through a fine, sintered-glass frit. The metal complexes were then isolated from the filtrate by precipitation with ether, hexanes, or MeOH.

Cu[Br$_4$Cav]$_2$(bime) (4). Using the general procedure described above, **4** was isolated as a brown powder in 60% yield from 150 mg of **2** after precipitation with hexanes. Mp: >300 °C. An analytical sample was obtained by slow diffusion of MeOH into a butyronitrile solution of the complex. Anal. Calcd for $C_{87}H_{82}Br_8CuN_4O_{17}\cdot 4CH_3(CH_2)_2CN$: C, 50.81; H, 4.55; N, 4.60. Found: C, 50.79; H, 4.80; N, 4.56.

Cu[Br$_4$Cav]$_2$(Me$_2$bpy) (5a). One hundred fifty mg of **2** gave, after precipitation with ether, **5a** as a brown powder in 75% yield. Mp: >300 °C. Anal. Calcd for $C_{88}H_{78}Br_8CuN_2O_{16}\cdot(CH_3CH_2)_2O$: C, 50.30; H, 4.04; N, 1.28. Found: C, 50.18; H, 4.29; N, 1.31.

Zn[Br$_4$Cav]$_2$(Me$_2$bpy) (5b). Complex **5b** was isolated from 170 mg as a pale yellow powder after precipitation with MeOH (66%). Mp: >300 °C. ^{1}H-NMR ($CDCl_3$): δ 1.50–1.70 (br m, 24H, CH_3 "feet"), 2.64 (br s, 6H, py CH_3), 3.61–3.97 (m, 12H, "inner" OCH_2), 4.29–4.78 (br m, 14H, "outer" OCH_2, CH), 5.45–5.53 (m, 6H, CH), 7.18 (br s, 4H, Ar H), 7.27 (s, 4H, Ar H), 7.49–7.56 (br m, 2H, py H), 8.14 (br s, 2H, py H), 9.07 (br s, 2H, py H). Anal. Calcd for $C_{88}H_{78}Br_8N_2O_{16}Zn\cdot 3H_2O$: C, 48.52; H, 3.89; N, 1.29. Found: C, 48.38; H, 3.89; N, 1.45.

Co[Br$_4$Cav]$_2$(Me$_2$bpy) (5c). Using 120 mg of **2**, the cobalt complex **5c** was obtained as a dark blue powder after precipitation with ether (73%). Mp: >300 °C. Anal. Calcd for $C_{88}H_{78}Br_8CoN_2O_{16}$: C, 49.91; H, 3.71; N, 1.32. Found: C, 49.99; H, 3.96; N, 1.52.

Ni[Br$_4$Cav]$_2$(Me$_2$bpy)$_2$ (6). The nickel complex **6** was prepared using the general procedure described above except that 1.0 equiv of Me_2bpy was used. Thus, **6** was obtained from 150 mg of **2** as a pale green powder after precipitation with cold (−20 °C) MeOH (80%). Mp: >300 °C. Anal. Calcd for $C_{100}H_{90}Br_8N_4NiO_{16}\cdot CH_3OH$: C, 51.98; H, 4.06; N, 2.40. Found: C, 52.26; H, 4.38; N, 2.63.

X-ray Crystallographic Structure Determination of 4. Brown crystals of **4** suitable for X-ray analysis were grown by slow diffusion of MeOH into a butyronitrile solution of the complex. Measurements were carried out on a crystal having the dimensions 0.20 × 0.20 × 0.20 mm using a Rigaku AFC-6S diffractometer and graphite-monochromatized Mo Kα radiation ($\lambda(K\alpha)$ = 0.709 30 Å) at −160 °C. Unit cell constants were derived from a least-squares refinement of 48 reflections in the range $25° < 2\theta < 32°$ (the θ-2θ scan technique was used to record intensities). A stationary count for one-tenth of the scan time at each end of the peak was used to correct for background counts. Peaks were subjected to profile analysis, and any portions of the scan not included in the peak were used to improve background estimates.

The structure was refined using full-matrix least-squares techniques. Only the copper and bromine atoms were refined anisotropically. The function minimized was $[\sum w(F_o - F_c)^2]^{0.5}$ with weights based on counter statistics. Calculations were performed using the NRCVAX system.[11] No correction was made for absorption. There are seven butyronitriles and one MeOH of solvation which are included with 100% occupancy. Crystal data are given in Table 1, and final atomic coordinates of selected atoms are given in Table 2.

Table 1. Crystallographic Data for Cu^{II}[Br$_4$Cav]$_2$(bime) (**4**)

formula	$C_{116}H_{133}Br_8CuN_{11}O_{18}$	α (deg)	110.091(21)
fw	2672.13	β (deg)	98.540(22)
T (°C)	−160	γ (deg)	103.922(21)
cryst system	triclinic	V (Å^3)	6002(3)
space group	$P\bar{1}$	Z	2
a (Å)	13.854(3)	ρ_{calc} (g cm^{-3})	1.479
b (Å)	21.602(5)	μ (mm^{-1})	3.05
c (Å)	22.743(6)	R,[a] R_w[b]	0.086, 0.094

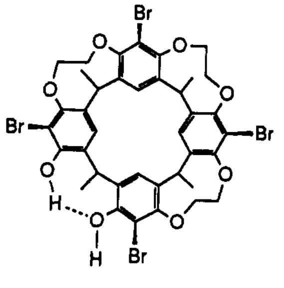
[a] $R = \sum(F_o - F_c)/\sum F_o$. [b] $R_w = [\sum(w(F_o - F_c)^2/\sum(wF_o^2)]^{0.5}$.

Table 2. Final Atomic Parameters for Selected Atoms in Cu[Br$_4$Cav]$_2$(bime) (**4**)

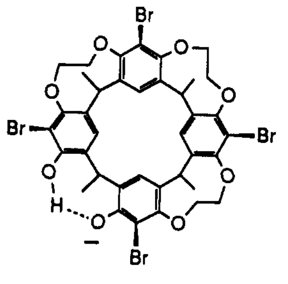
atom	x	y	z	B_{iso}, Å^2
Cu(1)	0.91128(22)	0.72550(15)	0.10033(14)	1.13(16)
N(11)	0.7618(15)	0.6912(10)	0.0539(9)	1.7(5)
N(21)	0.9401(14)	0.7685(9)	0.0383(9)	1.3(4)
O(101)	0.8857(11)	0.6884(7)	0.1668(7)	0.7(3)
O(201)	1.0564(11)	0.7563(7)	0.1407(7)	1.2(3)
O(177)	0.7672(11)	0.7382(8)	0.2348(7)	1.4(3)
O(277)	1.1547(11)	0.6910(7)	0.0627(7)	1.2(3)

Results and Discussion

Previous studies have shown that exposure of calixresorcinarene **1** to NaOH leads to formation of the tetraphenolate. Because of the H-bonding network about the octol rim, the remaining protons could not be removed with OH^- or CH_3O^-.[12] The same type of H-bonding is expected to be present in **2**, so selective formation of monoanion **3** should be possible. To determine the relative p*K*s of the two phenolic protons, we treated a solution of **2** in tetrahydrofuran (THF) with 1.0 equiv of lithium fluorenate,[13] which resulted in immediate discharge of the red color associated with the fluorenate anion. However, the color was not discharged upon addition of a second equivalent of lithium fluorenate, indicating no reaction with the second phenolic proton. The cavitand dianion *can* be formed by stirring **2** with an excess of NaH in *N*,*N*-dimethylformamide (DMF). Upon addition of fluorene to a filtered solution of the dianion, the solution turned red, indicating deprotonation of fluorene. This sets the lower limit for the p*K* of the second proton at 23.



2



3

Because the two phenolic protons possess such disparate acidities, it seemed likely that the cavitand might function as a monodentate, monoanionic ligand, **3**. An auxiliary ligand could be added to complete the coordination sphere of the metal ion.

---

(7) (a) Sorrell, T. N.; Pigge, F. C. *J. Org. Chem.* **1993**, *58*, 784–785. (b) Sorrell, T. N.; Richards, J. L. *SynLett* **1992**, 155–156.

(8) Cram, D. J.; Karbach, S.; Kim, H.-E.; Knobler, C. B.; Maverick, E. F.; Ericson, J. L.; Helgeson, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 2229–2237.

(9) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986; p 3.

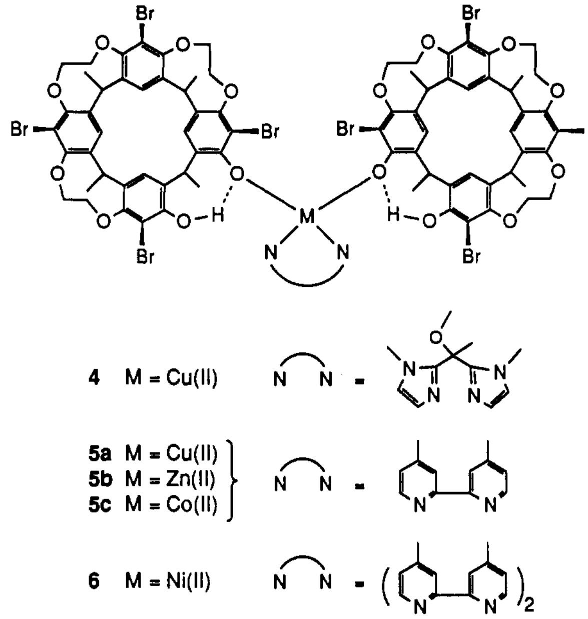
(10) Abbreviations used in this paper: bime, 1,1-bis(1-methylimidazol-2-yl)-1-methoxyethane; DMF, *N*,*N*-dimethylformamide; Me_2bpy, 4,4′-dimethyl-2,2′-bipyridine; MeOH, methanol; THF, tetrahydrofuran.

(11) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384–387.

(12) Schneider, H.-J.; Güttes, D.; Schneider, U. *J. Am. Chem. Soc.* **1988**, *110*, 6449–6454.

(13) This was generated by mixing equimolar amounts of fluorene (p*K* 23) and *n*-butyllithium in THF.

Chart 1



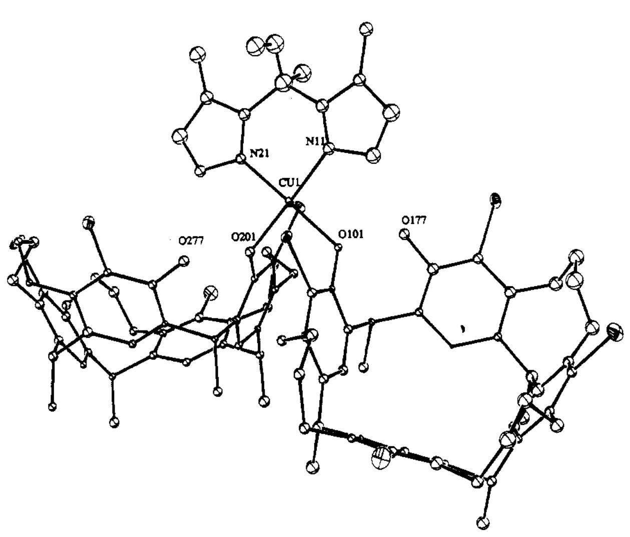


Figure 1. Structure of Cu[Br_4Cav]$_2$(bime) (**4**) showing 30% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu(1)–N(11), 2.007(19); Cu(1)–N(21), 1.976(19); Cu(1)–O(101), 1.976(14); Cu(1)–O(201), 1.928(15); N(11)–Cu(1)–N(21), 88.4(8); N(11)–Cu(1)–O(101), 93.3(7); N(21)–Cu(1)–O(201), 89.8(7); O(101)–Cu(1)–O(201), 88.7(6); N(11)–Cu(1)–O(201), 177.0(7); N(21)–Cu(1)–O(101), 176.4(7).

The syntheses of metal complexes **4**–**6** were subsequently carried out (Chart 1).

Crystals of **4** were grown by slow diffusion of MeOH into a butyronitrile solution of the complex, and the structure of **4** is shown in Figure 1. The geometry about the Cu(II) center is square planar, and the bond distances and angles are similar to those reported for related structures such as Cu^{II}[salen][14] and Cu(II) complexes derived from catechols and bidentate amines.[15] Thus, the Cu-N and Cu-O bond distances are all between 1.9 and 2.0 Å, as expected; but O(177) and O(277) are too far away from the copper ion (3.86 and 3.78 Å, respectively) to participate in any type of bonding interaction. The angles between adjacent donors are close to 90°; furthermore, the N(11)–Cu(1)–O(201) and N(21)–Cu(1)–O(101) angles are close to the expected 180°. Within error, the Cu(II) ion sits in the plane of the ligating atoms.

Within the cavitand itself, the O(101)–O(177) and O(201)–O(277) distances are both ~2.6 Å, which is within the range for a hydrogen bond between phenolic OH groups.[16] On the other hand, the rigid structure of the cavitand framework may be responsible for the proximity of those oxygen atoms, and the illustrated hydrogen bond may not actually exist. Seven butyronitriles and one MeOH molecule are present as solvates for each molecule of **4**. None, however, were found within the cavity of the macrocycle.[17]

The EPR spectra of **4** ($g_\parallel$ = 2.28, $A_\parallel$ = 170 G, $g_\perp$ = 2.08) and **5a** ($g_\parallel$ = 2.27, $A_\parallel$ = 170 G, $g_\perp$ = 2.09) are both consistent with tetragonal coordination about the Cu(II) ion.[18] The absorption spectrum of **5a** shows λ_{max} = 285 nm (ϵ = ~33 000 M^{-1} cm^{-1}) which we assign to intraligand $\pi \rightarrow \pi^*$ transitions because this feature is also present in the spectrum of the Zn(II) complex **5b**. The spectrum of **5a** also possesses a broad absorbance centered at 456 nm (ϵ = 2330 M^{-1} cm^{-1}) which we tentatively assign as a phenolate → Cu(II) CT band in accordance with other studies involving Cu(II)–phenoxide complexes.[19] The expected weak Cu(II) d–d transitions are not observed, presumably obscured by the broad absorbance at 456 nm. The Co(II) complex, **5c**, also appears to be square planar on the basis of its magnetic moment of 2.79 μ_B.[20] Its absorption spectrum is similar to that of the copper(II) analog and displays λ_{max} = 285 nm (ϵ = 27 000 M^{-1} cm^{-1}) and a second, weaker absorbance at λ = 461 nm (ϵ = 4000 M^{-1} cm^{-1}).

In contrast, Zn(II) complex **5b** most likely has a tetrahedral geometry in keeping with the structures of other Zn complexes.[21] An ^{1}H-NMR spectrum of **5b**, while somewhat broadened, clearly shows a ratio of 1:2 between dimethylbipyridine and cavitand. The Ni(II) compound, **6**, which is octahedral, has a magnetic moment μ_{eff} = 3.79 μ_B.[22]

This study demonstrates the feasibility of using partially-unlinked cavitands as ligands for a variety of transition metal ions. The placement of the metals in the cavitand framework, coupled with the ability of these macrocycles to act as size- and charge-selective hosts for small organic molecules, creates the possibility of developing catalysts for selective transformations of bound substrate, and studies along these lines are currently in progress. Additionally, the metal ion in the complexes described above also serves to link two cavitand molecules. The coupling of two cavitands *via* the upper rim to form carcerands[23] and the coupling of two partially-linked cavitands through aromatic spacers[24] have been previously described. These types of molecules have been found to possess interesting properties with regard to molecular recognition and host–guest chemistry. Utilizing transition metals as bridging moieties (as in **4**–**6**) illustrates a

---

(14) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385–403.

(15) (a) Buchanan, R. M.; Wilson-Blumenberg, C.; Trapp, C.; Larsen, S. K.; Greene, D. L.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3070–3076. (b) Thompson, J. J.; Calabrese, J. C. *Inorg. Chem.* **1985**, *24*, 3167–3171.

(16) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Co.: San Francisco, CA, 1960; p 272 and references therein.

(17) In the majority of cavitand structures, a solvate molecule is found within the cavity. See ref 8 for several examples.

(18) Solomon, E. I.; Baldwin, M. J.; Lowrey, M. D. *Chem. Rev.* **1992**, *92*, 521–542 and references therein.

(19) (a) Ainscough, E. W.; Bingham, A. G.; Brodie, A. M.; Husbands, J. M.; Plowman, J. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1701–1707. (b) Prados, R.; Boggess, R. K.; Martin, R. B.; Woodworth, R. C. *Bioinorg. Chem.* **1975**, *4*, 135–142. (c) Bullock, J. I.; Hobson, R. J.; Povey, D. C. *J. Chem. Soc., Dalton Trans.* **1974**, 2037–2043.

(20) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th Ed.; John Wiley & Sons: New York, 1980; p 772.

(21) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447–454.

(22) An analogous high-spin complex having the coordination environment Ni(N)$_4$(OAr)$_2$ has been prepared using bipyridine and 2,2′-biphenol: Andrä, K.; Fleischer, F. *Z. Anorg. Allg. Chem.* **1982**, *485*, 210–216.

(23) Cram, D. J.; Blanda, M. T.; Paek, K.; Knobler, C. B. *J. Am. Chem. Soc.* **1992**, *114*, 7765–7773 and references therein. See also: Timmerman, P.; van Mook, M. G. A.; Verboom, W.; van Hummel, G. J.; Harkema, S.; Reinhoudt, D. N. *Tetrahedron Lett.* **1992**, *33*, 3377–3380.

(24) Cram, D. J.; Tunstad, L. M.; Knobler, C. B. *J. Org. Chem.* **1992**, *57*, 528–535.

new way of coupling the cavitand framework. Although the two macrocycles in **4** appear to be unable of acting cooperatively to recognize and bind a potential guest, variation of the appendages along the lower rim of the cavitand, as well as the auxiliary ligand, could lead to cooperative guest binding. Finally, syntheses of metallocavitands in which the cavitand acts as a bidentate bis(phenoxy) ligand are also under investigation.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the National Science Foundation (Grant CHE 9100280), to the Burroughs-Wellcome Fund (FCP), and to the Department of Education (FCP) for financial support of this work. We are very grateful to Dr. William E. Hatfield and Dr. Zurong Shi for obtaining the EPR spectra and to Bill Kalsbeck and Dr. C. Cornman at North Carolina State University for their assistance in obtaining the magnetic moments.

Supplementary Material Available: A figure showing the atom-labeling scheme and tables summarizing crystallographic data and anisotropic thermal parameters for **4** (3 pages). Ordering information is given on any current masthead page.