indeed be stabilized by the interaction with a second transition-metal center.

A more complete account of the synthetic and crystallographic details will appear at a later date.

Acknowledgment is made to the Swiss National Science Foundation for support of this research.

Registry No. 1a, 14243-64-2; **1b**, 15529-90-5; **2a**, 83527-78-0; **2b**, 83527-79-1; **3**, 18660-47-4; **4a**, 83527-81-5; **4b**, 83527-83-7; **5**, 83527-85-9; **6**, 83527-86-0.

Supplementary Material Available: Positional parameters and thermal factors for the cation $[(PPh_3)Au(\mu\text{-}H)IrH_2(PPh_3)_3]^+$ (3 pages). Ordering information is given on any current masthead page.

Hemispherands Containing Cyclic Urea and Anisyl Units[1]

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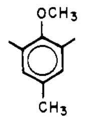
Previous papers demonstrated that the spherands owe their superior alkali metal ion binding and selecting properties to the presence in the hosts prior to complexation of enforced cavities lined with electron pairs.[2] Crystal structure determinations demonstrated that the cavities of chorands and cryptands are filled with inward turned methylene groups that must be displaced by incoming ions during complexation.[3] Hemispherands are hosts at least half of whose cavity structures are organized for complexation during synthesis rather than during complexation. We report here the syntheses and binding properties of hemispherands **2–6** (Chart I) and the crystal structures of **4** and its t-BuNH$_3$ClO$_4$ complex. Because of their awkward names, hosts **1–6** and their precursors are referred to by combinations of letters, each of which stands for a binding unit. The code is indicated and is illustrated by the sequence A(AD)$_2$D for **1** (Chart I), whose synthesis, binding properties,[4] and crystal structure (and that of its t-BuNH$_3^+$ complex) have been reported.[3] The syntheses of **2–6** are outlined in the supplementary material. All new compounds gave elemental analyses within 0.30% of theory and ^{1}H NMR and mass spectra compatible with their assigned structures.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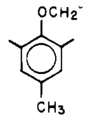
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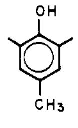
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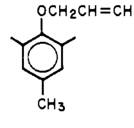
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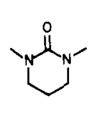
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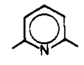
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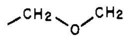
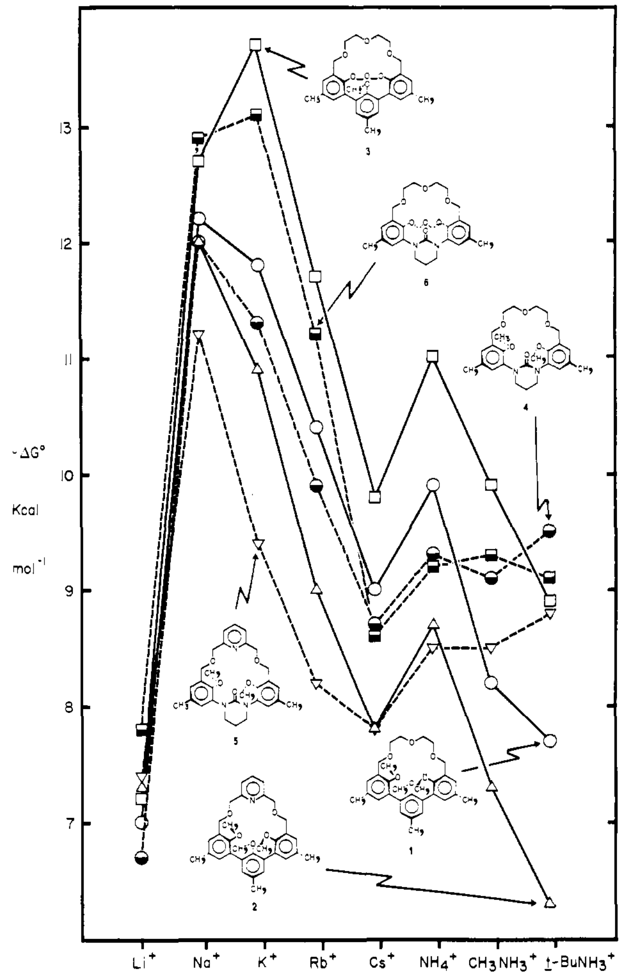

D

Chart I



Drawing **7** depicts the preliminary crystal structure of free host U(AD)$_2$D (**4**), and **8** that of its complex, U(AD)$_2$D·t-BuNH$_3^+$. Notice that the A–U–A units in **7** and **8** possess essentially the same organization. The two anisyl oxygens are on the side of the macroring opposite to that of the urea oxygen, and the unshared electron pairs of the three oxygens line a half cavity. In the free host **7**, the unshared electron pairs of the three oxygens of the D–D–D unit diverge from the cavity, which is filled with inward-turned hydrogens of two CH$_2$ groups, as is observed in the crystal structures of numerous chorands.[3] Upon complexation, these hydrogens are displaced from the cavity, and the unshared electron pairs of the three oxygens in the complex converge on the cavity. Thus some organizational burden with respect to the *chorand part* of the host is placed on the guest during complexation, as has been observed with A(AD)$_2$D (**1**) complexing t-BuNH$_3^+$.[3] As expected from CPK molecular model examination of U(AD)$_2$D·t-BuNH$_3^+$ prior to its synthesis, the t-BuNH$_3^+$ group hydrogen bonds the urea and the two benzyloxy oxygens in a tripod arrangement to provide the perching complex indicated in **8**. This tripod binding is possible only when the guest occupies that face of the macroring that is anti to the oxygens of the two anisyl units. The opposite face is occupied in the A(AD)$_2$D·t-BuNH$_3^+$ complex.[3] As expected, in **8** the C–C–N–H dihedral angles are close to 60°, and this C–N bond is essentially normal to the plane of the three hydrogen-bonded oxygens.

The t-BuNH$_3^+$ClO$_4^-$ complexes in CDCl$_3$ solution of U(AD)$_2$D (**4**), U(AD)$_2$P (**5**), and A'(U)(D)(DDD)A' (**6**) must resemble each other since in their ^{1}H NMR spectra, the signals of the guests' CH$_3$ groups are moved upfield to δ 0.644, 0.503, and 0.78, respectively. Model examination of all three complexes indicate the CH$_3$ groups are located in the shielding cones of two or three aryl groups. In contrast, for the t-BuNH$_3^+$ complex of A(AD)$_2$D

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[1] We thank the Division of Basic Sciences of the Department of Energy for the contract (AT(04-3), P.A. 218) that supported all of the research except the crystal structure work, for which we thank the National Science Foundation, Grant NSF CHE 80-22525.

[2] (a) Cram, D. J.; Lein, G. M.; Kaneda, T.; Helgeson, R. C.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 6228–6232. (b) Lein, G. M.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1982**, 301–304.

[3] Cram, D. J.; Trueblood, K. N. *Top. Curr. Chem.* **1981**, *98*, 43–106.

[4] Koenig, K.; Lein, G. M.; Stückler, P.; Kaneda, T.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553–3566.

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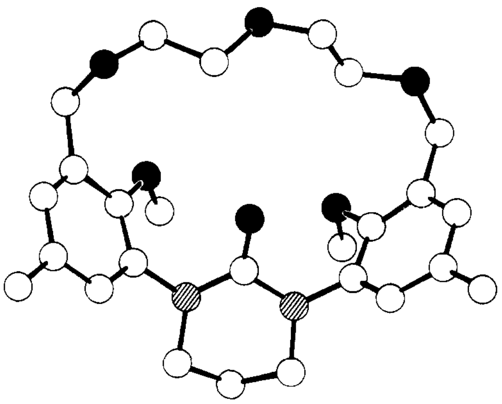
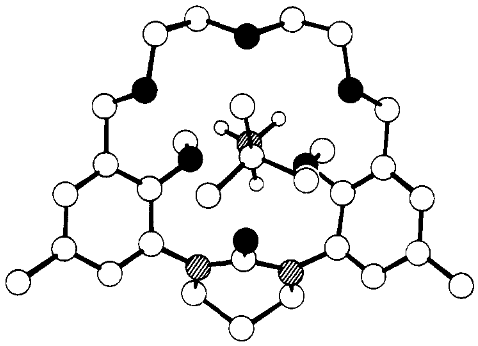


7, U(AD)$_2$D



8, U(AD)$_2$D·t-BuNH$_3^+$

(1), the CH_3 groups are found at δ 1.43. In models of this complex, the methyls are far removed from all aryl groups since the guest complexes from the face opposite to that of the hosts containing the urea unit.[3]

The free energies were determined for hemispherands **1–6** binding the alkali metal, ammonium, and alkylammonium picrates in $CDCl_3$ saturated with D_2O.[5] The $-\Delta G°$ values were determined by extracting 0.05 or 0.001 M salt solutions in D_2O with solutions of hosts in $CDCl_3$ at 25 °C.[2b]

The profiles in Chart I of the six hosts generally correlate their structures and complexing properties to provide the following conclusions. (1) As a class the hemispherands are better binders by several kcal mol^{-1} than 2,3-naphtho-18-crown-6, whose $-\Delta G°$ values (kcal mol^{-1}) for the picrate salts are as follows: Li^+, 5.9; Na^+, 8.3; K^+, 10.8; Rb^+, 9.6; Cs^+, 8.3; NH_4^+, 9.5; $CH_3NH_3^+$, 7.5; t-$BuNH_3^+$, 6.9.[4] The $C_6H_5OCH_3$ unit is intrinsically poorer as a ligand than the CH_2OCH_2 unit, but this property is more than compensated for by the self-organization for complexation of three adjacent anisyl groups. (2) The binding profiles of the three hemispherands containing three anisyl units resemble those of their corresponding analogues in which a cyclic urea unit is substituted for the central anisyl unit. This generalization applies to all guests except $CH_3NH_3^+$ and t-$BuNH_3^+$. As models suggested and crystal structure comparisons bore out, two attached anisyl groups organize the cyclic urea unit for binding in a way similar to the way they organize a central anisyl group. (3) Rigidification of the hosts and augmentation of the number of ligating sites by incorporation of the extra bridge in A′(A)(D)(DDD)A′ (**3**) and A′(U)(D)(DDD)A′ (**6**) generally improve binding, particularly toward K^+ and t-$BuNH_3^+$. These two hosts slightly favor complexation of K^+ over Na^+, but the four more flexible hosts favor Na^+ over K^+ by varying degrees. (4) Substitution of a pyridine for a CH_2OCH_2 unit[5] reduces complexation toward all ions except for the case of U(AD)$_2$P (**5**) binding $CH_3NH_3^+$ and t-$BuNH_3^+$. It also enhances the favored binding of Na^+ over that of K^+. (5) The hosts containing the urea units are particularly good complexers of $CH_3NH_3^+$ and t-$BuNH_3^+$, providing values that range from 8.5 to 9.5 kcal mol^{-1}.

This study demonstrates that the hemispherands are a family of hosts with binding properties in between those of the chorands and the spherands.[2] Employment of an organized urea ligating site greatly expands the number of structural options available to the designer of host–guest complexes.

Supplementary Material Available: Preparation of hemispherands **2–6** (3 pages). Ordering information is given on any current masthead page.

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(5) Slightly different and more accurate values are given here for **1** than were reported previously[1] and resulted from using the lower concentration of aqueous picrate salt concentrations when the $-\Delta G°$ values exceeded 10 kcal mol^{-1}.

Spherand Hosts Containing Cyclic Urea Units[1]

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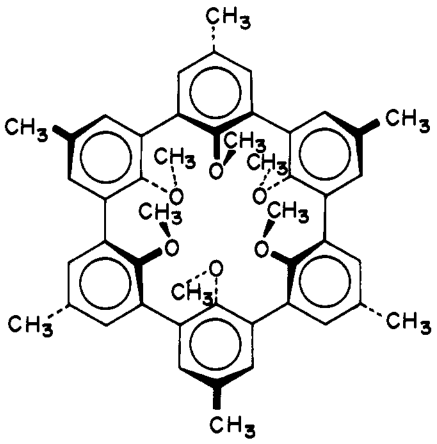
Earlier work demonstrated that the spherands, of which **1** is



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the prototype, are highly selective and powerful binders of Na^+ and Li^+.[2] Since anisyl units are intrinsically poor ligands for complexing ions, the enforced, ideal organization of the oxygens in **1** prior to complexation is responsible for the host systems' unique complexing properties.[3] The oxygens of urea units should be generally superior ligands to those of anisyl oxygens.[4] Examination of molecular models (CPK) of six-membered cyclic urea units indicated they might be substituted for some of the anisyl units of **1** to produce hosts whose oxygens are also organized during synthesis rather than during complexation. This paper reports the syntheses, binding properties, and structures of new spherand hosts **2–5** (Chart I), which combine cyclic urea and anisyl binding units with appropriate hydrocarbon spacer units (CH_2 or o-$CH_2C_6H_4CH_2$). Sequences of capital letters will specify the formulas, in which A stands for 2,6-disubstituted anisyl, A′ for

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[1] We thank the National Science Foundation for Grant NSF CHE 81-09532 and Grant NSF CHE 80-22525 and the Public Health Service for Grant GM 12640, which supported this research.

(2) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 6752–6754.

(3) (a) Trueblood, K. N.; Knobler, C. B.; Maverick, E.; Helgeson, R. C.; Brown, S. B.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 5594–5596. (b) Cram, D. J.; Lein, G. M.; Kaneda, T.; Helgeson, R. C.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *Ibid.* **1981**, *103*, 6228–6232. (c) Lein, G. M.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1982**, 301–304.

(4) (a) Mitsky, J.; Jaris, L.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 3442–3445; (b) Atkins, H. W.; Gilkerson, W. R. *Ibid.* **1973**, *95*, 8551–8559.

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