is electron-precise (12 electrons) while $[Mo_4S_4(edta)_2]^{3-}$ and $[Mo_4S_4(NCS)_{12}]^{7-}$ are species[7,10] with 11-electron counts and $[Mo_4S_4(Et_2NCS_2)_6]$ has 10 electrons.[12] The 12-electron species has essentially $T_d$ symmetry, while $[Mo_4S_4(edta)_2]^{3-}$ has Mo–Mo distances ranging from 2.755 to 2.880Å,[10] and the 10-electron species has distances to 2.732 (5) (2×) and 2.861 (16) Å (4×).

We wish to report the preparation of the $Mo_4S_4^{6+}(aq)$ ion and a compound derived therefrom, $(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O$, which are important in the context of the facts just summarized for two reasons. They are 10-electron species not constrained by any bridging ligands and the method of preparation differs from all those used previously to make $Mo_4S_4$ containing compounds. In our recent report[6] of the preparation of the $Mo_3S_4^{4+}(aq)$ ion by refluxing a mixture of $Mo(CO)_6$ and $Na_2S$ in acetic anhydride, followed by aqueous workup employing a cation exchange resin, we noted that in addition to the dark green $Mo_3S_4^{4+}(aq)$ ion there was a second, paler green ion (denoted II) that adhered more firmly to the resin. From the eluate containing this second green ion we have been able to crystallize the compound $(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O$ and determine its structure.[19] The structure of the tetranuclear anion is shown in Figure 1.

The $[Mo_4S_4(NCS)_{12}]^{6-}$ ion resides on a crystallographic site of $3m$ ($C_{3v}$) symmetry. Instead of the $T_d$ symmetry potentially possible for this cuboidal species, it has only $C_{3v}$ symmetry, as can be seen clearly in the Mo–Mo distances. The $Mo_4$ unit is a triangular pyramid, with slant edges of length 2.791 (1) Å and basal edges of length 2.869 (1) Å. Each face of the pyramid is capped by a sulfur atom and each molybdenum atom has three N-bonded thiocyanate ions attached to it.

The green solution eluted from the cation exchange column with 2 M HCl is believed to contain the $Mo_4S_4^{6+}(aq)$ ion, whose absorption spectrum is shown in Figure 2, along with the spectra of the $Mo_3S_4^{4+}(aq)$ and $[Mo_4S_4(NCS)_{12}]^{6-}$ ions.

The pronounced distortion of the $Mo_4$ cluster in the $[Mo_4S_4(NCS)_{12}]^{6-}$ ion from $T_d$ to $C_{3v}$ symmetry requires an explanation. It seems unlikely to us that this is due to intermolecular (packing) forces. A molecular orbital calculation (Fenske–Hall method[20]) shows that the HOMO of a $[Mo_4S_4(NCS)_{12}]^{8-}$ ion ($12e^-$) would be a fully occupied $t_2$ orbital. For a $C_{3v}$ distortion of the type observed in the $[Mo_4S_4(NCS)_{12}]^{6-}$ ion ($10e^-$), the $t_2$ orbital is split into a lower, filled e orbital and an upper, empty $a_2$ orbital. These results support (but do not prove) our view that the $10e^-$ system undergoes a Jahn–Teller distortion along one coordinate of a $T_2$ vibration, thus splitting the degeneracy of the $t_2$ orbitals.[21]

During our preparation we observed a most interesting chemical interconversion of the $Mo_3S_4$ and the $Mo_4S_4$ cores. While the $Mo_3S_4$ species have previously been described as incomplete cubes, the topological similarity of the two species does not a priori necessitate a chemically tractable reaction pathway between the two. We now find that the cubane aquo ion is converted to the $Mo_3S_4$ trimer aquo ion by simple air oxidation. If solutions of the purified second ion (eluted with 4 M HCl and diluted to 0.4 M) are rechromatographed after exposure to air the $Mo_3S_4$ aquo species is isolated together with unreacted $Mo_4S_4$. In the presence of ligands that stabilize the trimer, such as oxalate, complete conversion is achieved within 2 days.

**Acknowledgment.** We thank the National Science Foundation for support.

**Registry No.** $(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O$, 98759-94-5; $Mo(CO)_6$, 13939-06-5.

(18) The $(\eta^5\text{-}C_5H_5)_4Mo_4S_4^{0,+1,+2}$ species form the only set in which exact stoichiometric analogues with differing electron counts are known so far. Cf.: Bandy, J. A.; Davies, C. E.; Green, J. C.; Green, M. L. H.; Prout, K.; Rodgers, D. P. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1395.

(19) Crystallographic data: Hexagonal, $P6_3mc$, $a$ = 17.500 (3) Å, $c$ = 10.275 (2) Å, $Z$ = 2, $R$ = 0.030, $R_w$ = 0.041. One hundred and eleven parameters were refined using 1049 independent reflections with $F_o^2 > 3\sigma(F_o^2)$.

(20) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(21) The significance of the previous observation of a $D_{2d}$ distortion in a $10e^-$ system[12] is uncertain because the two short Mo–Mo distances are bridged by dithiocarbamate ligands.

**Supplementary Material Available:** A table of fractional coordinates and a table summarizing the crystallographic study (2 pages). Ordering information is given on any current masthead page.

## Synthetic Receptors: Size and Shape Recognition within a Molecular Cleft

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Because the idea is prevalent that host–guest chemistry can be a useful model for substrate–receptor biochemistry, bioorganic chemists have developed a number of systems capable of reversible binding interactions for such studies. Macrocyclic compounds such as polyethers,[1] cyclodextrins,[2] and cyclophanes[3] have dominated this area, presumably because their interactions with smaller molecules are easily conceptualized. We recently introduced[4] synthetic structures featuring a *molecular cleft* and here give evidence of their unusual binding properties. In these compounds carboxyl derivatives converge to provide *receptors* for molecules of complementary size, shape, and hydrogen-bonding capacity.

The new molecules are prepared by the condensation of the triacid[5] **1** with appropriate aromatic diamines such as the dye acridine yellow (**2**) (eq 1). The resulting diacid functions of **3** are constrained to the relative orientation shown; the aliphatic methyl groups prevent epimerization of the carboxyls while the aromatic methyls prevent rotation about the $C_{aryl}$–$N_{imide}$ bonds. Molecular mechanics calculations and CPK models indicate a distance of about 8 Å between the opposing carboxyl oxygens of **3**, and the estimates are supported by its binding behavior toward appropriate diamines.

For example, in $CDCl_3$ the NMR signal of $H_4$ and $H_5$ moves *upfield* (>0.5 ppm) in the presence of pyrazine **4**, whereas with bases of inappropriate size (4,4′-bipyridyl, pyridine, or triethylamine) only conventional acid/base chemistry occurs, and this signal moves downfield 0,2 ppm. A stoichiometric complex of **3** with diazabicyclooctane (DABCO) was also observed.[6] In general, complexation rates were rapid at room temperature; an activation barrier ($\Delta G^{\ddagger}_c$) of 10.5 kcal/mol was determined for the exchange of DABCO between molecules of **3** at $T_c$ = 208 K.

Binding of **3** of diketopiperazines of simple amino acids was also observed, but with molecules of inappropriate shape (uracil) or hydrogen-bonding capabilities (sarcosine anhydride) no complexes were formed. The diamide **6**, mp >340 °C, prepared from **3** with $SOCl_2$ followed by $NH_3$,[8] also showed binding to diketo-

(1) See, for example: Top. Curr. Chem. **1981**, *98*. Cram, D. J. *Science (Washington, D.C.)* **1983**, *219* 1177–1183. Lehn, J.-M. *Ibid.* **1985**, *227*, 849–856.

(2) Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry"; Springer-Verlag: New York, 1978.

(3) Stetter, H.; Roos, E.-E. *Chem. Ber.* **1955**, *88*, 1390, 1395. Odashima, K.; Itai, A.; Iitaka, Y.; Koga, K. *J. Am. Chem. Soc.* **1980**, *102*, 2504. Miller, S. P.; Whitlock, H. W., Jr. *Ibid.* **1984**, *106*, 1492. Winkler, J.; Coutouli-Argyropoulou, E.; Leppkes, R.; Breslow, R. *Ibid.* **1983**, *105*, 7198. Diederich, F.; Griebel, D. *Ibid.* **1984**, *106*, 8037.

(4) Rebek, J.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.*, in press.

(5) Kemp, D. S.; Petrakis, K. S., *J. Org. Chem.* **1981**, *46*, 5140.

(6) All complexation studies were performed in $CDCl_3$, and chemical shift changes in NMR signals of receptor or substrate were plotted against relative concentrations. Clean breaks in the plots were observed at the stoichiometries reported. Association constants were obtained by Hildebrand–Benesi[7] treatment of the data. For **3** + DABCO $K_a = 1.1 \times 10^5$ $M^{-1}$; for complex **7** $K_a = 1.8 \times 10^4$ $M^{-1}$.

(7) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.

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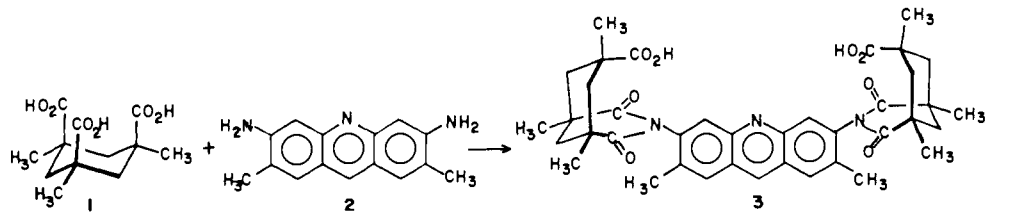

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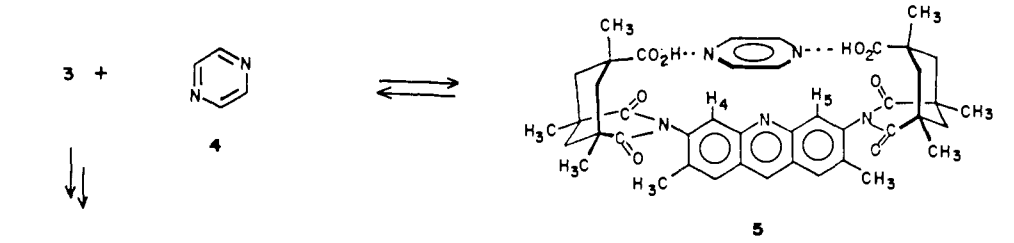

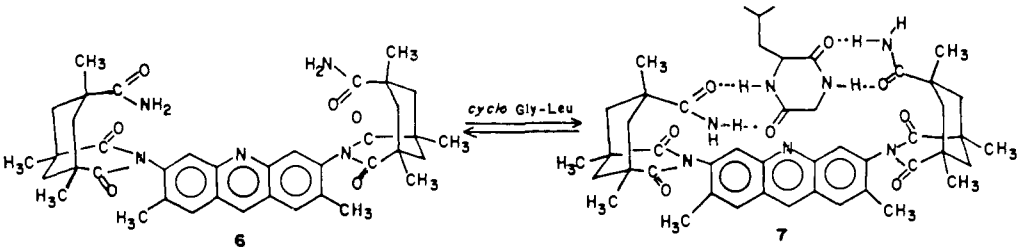

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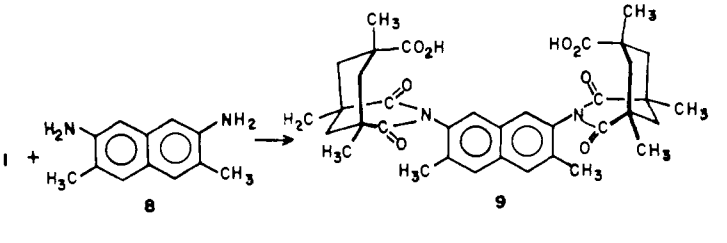

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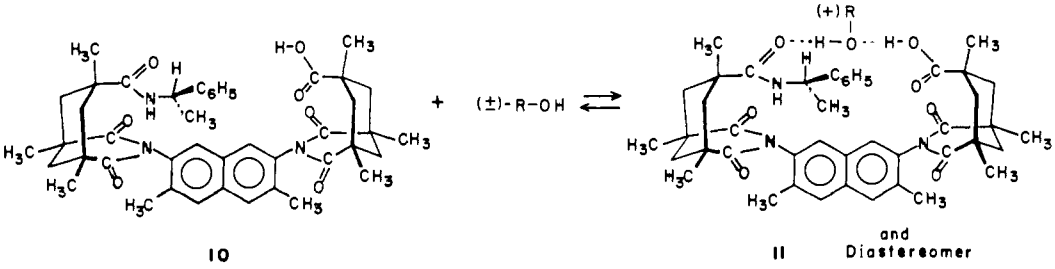

(4)

piperazines such as *cyclo*-Gly-Leu. While only crystallographic analysis can establish the structural details involved in the complexes, a reasonable interpretation of these studies is offered in Eq 2. The dimensions and the stereoelectronics for bonding of the receptors **3** and **6** are matched by the substrates in the production of the supermolecular complexes **5** and **7**.

A smaller cleft is available from the condensation product of **1** with the naphthalenediamine[4] **8** (eq 3). In **9**, about 5.5 Å separates the opposing carboxyl oxygens and tenacious binding results to substrates that bridge this gap. Complexation occurs with alcohols and amines (2:1); diols, diamines, or amino alcohols form 1:1 complexes. In addition, the monoamide **10** has been prepared in which an asymmetric environment confronts a carboxylic acid. This substance behaves as a *chiral solvating agent*[9] for the NMR spectroscopy of racemic alcohols such as (±)-α-phenylethanol or (±)-menthol. This effect arises from the formation of diastereomeric complexes, e.g., **11**, under conditions of rapid exchange (eq 4).

The hydrogen-bonding abilities of these rigid structures provide a complement to the ionic binding forces generally involved with macrocyclic polyethers and the hydrophobic interactions which characterize cyclodextrins and related structures.[10] In addition to their topology and mode of binding, the structures reported here differ from macrocyclics in another, more subtle sense. It has been difficult to attach auxiliary functional groups to macrocycles in a catalytically useful manner; i.e., in the sense that functional groups converge to define the active sites of enzymes. The new structures may be useful in this regard since they resemble the aspartic proteinases[11] and lysozyme[12] both of which feature two

(8) All new substances were characterized by a full complement of high-resolution spectra and/or elemental analyses.

(9) Weisman, G. R. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 1 Chapter 8. For example, two molecules of isopropyl alcohol were retained by **9** in the solid state after exposure to reduced pressure overnight. For **9** with dimethyl tartrate $K_a = 10^3\ M^{-1}$; $\Delta\nu$ for diastereomeric complexes **11** (using 20% **10**) were 10 Hz in α-phenylethanol ($CH_3$) and 5 Hz in menthol (C*H*OH).

(10) For a recent, relevant discussion of hydrogen bonding see: Fersht, A. R.; Shi, J.-P.; Knill-Jones, J.; Lowe, D. M.; Wilkinson, A. J.; Blow, D. M.; Brick, P.; Carter, P.; Waye, M. M. Y.; Winter, G. *Nature (London)* **1985**, *314*, 235–238.

(11) Pearl L.; Blundell, T. *FEBS Lett.* **1984**, *174*, 96–101.

(12) Blake, C. C. F.; Koenig, D. F.; Mair, G. A.; North, A. C. T.; Phillips, D. C.; Sarma, V. C. *Nature (London)* **1965**, *206*, 757.

carboxyl groups converging at their active sites. However, the intrinsic value of the new structures derives from their rigidly maintained shape, a feature that permits examination of stereoelectronic effects of *carboxyl oxygen*[13] for the first time. We shall report on these experiments in due course. In the meantime, we note that peracid derivatives of such structures have shown unprecedented selectivity in olefin epoxidation reactions.[14]

**Acknowledgment.** We are indebted to the National Science Foundation for support and to Professor K. N. Houk and D. Spellmeyer for structural computations.

(13) Gandour, R. *Bioorg. Chem.* **1981**, *10*, 169-176.
(14) Rebek, J.; Marshall, L.; Wolak, R.; McManis, J. *J. Am. Chem. Soc.* **1984**, *106*, 1170-1171.

## Molecular Recognition: Three-Point Binding Leads to a Selective Receptor for Aromatic Amino Acids

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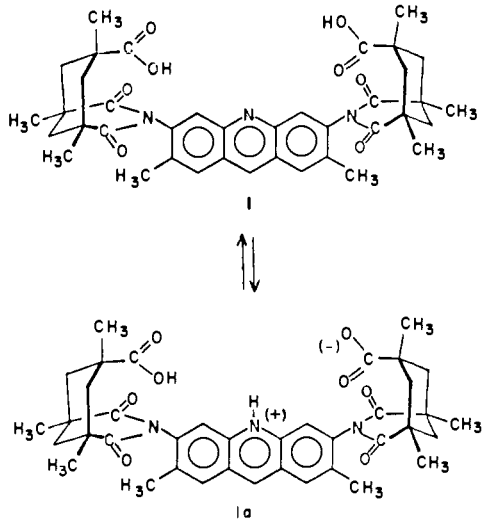
In a recent disclosure we introduced the acridine derivative **1** and described its binding behavior.[1] It features a rapidly assembled and rigidly maintained molecular cleft into which molecules of complementary size, shape, and hydrogen-bonding capacity are bound. Because NMR spectra of **1** indicate the presence of its zwitterionic form, **1a**, eq 1, it appeared probable




(1)

that molecules of complementary charge could also be bound within its cleft. In fact, phenylalanine, tryptophan, and tyrosine O-methyl ether[2] were extracted from their aqueous solutions with high efficiency by **1** into $CDCl_3$; NMR spectroscopy indicated that these amino acids occupied nearly 50% of the available receptor molecules **1**.

The sheer lipophilicity of these amino acids can only be partially responsible for their recognition by **1** since leucine, isoleucine, and valine, which show even less affinity for water,[3] were not extracted

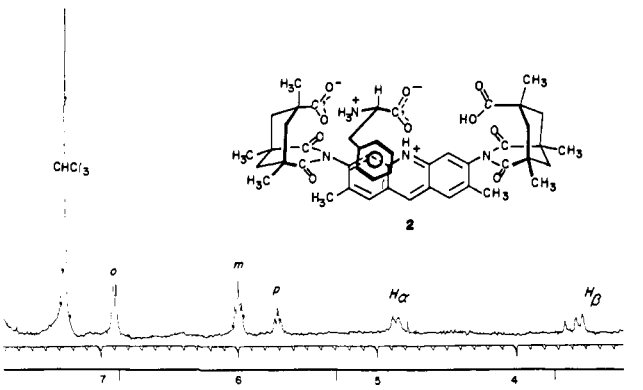
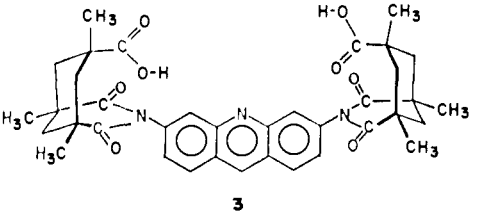
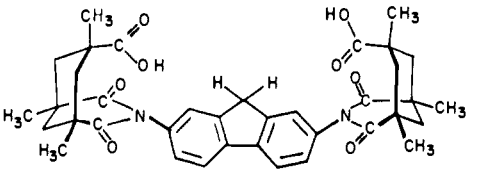



**Figure 1.** Portion of the 300-MHz NMR spectra of phenylalanine in contact with **1** in $CDCl_3$. Structure **2** is proposed.

to any appreciable extent. Rather, more specific interactions of the aromatic residues with the acridine nucleus must provide the selectivity. The NMR spectrum of the phenylalanine complex is reproduced below; the dramatic upfield shifts of the phenyl protons are most easily rationalized by the stacking interactions, perhaps of a charge-transfer nature, in the structure **2** proposed in Figure 1. Similar spectra were observed with tryptophan and the tyrosine derivative, but no evidence for extraction of phenylglycine was obtained. Inspection of CPK models reveals that this last amino acid is unable to achieve the stacking interaction while maintaining the charge-charge interactions and their attendant hydrogen bonds within the cleft.

The convergence of the functional groups of the receptor also appears to be an important factor in complex formation. Extraction studies with **3**, in which rotation about the $c_{aryl}$-$N_{imide}$




bond is possible,[4] show complexation with these aromatic amino acids is much reduced (10-20% as efficient as with **1**) but still of the same stacking nature. The fluorene derivative **4**, lacking both zwitterionic character and a well-placed aromatic ring, showed no evidence of binding to these amino acids at all. Thus structure **2** is supported by all of the available evidence, but a 2:1 complex (diacid/amino acid) is also possible.

The binding specificity of **1** and its ability to extract amino acids with such efficacy is unique. Such species have frequently been transported across liquid membranes as ammonium salts by crown ethers and detergents[5] or as carboxylates by other phase-transfer agents. Binding and transport of the actual zwitterionic forms has been disappointing. For example, Pederson[6] noted complex

(1) Rebek, J.; Askew, B.; Islam, N.; Killoran, M.; Nemeth, D.; Wolak, R. *J. Am, Chem. Soc.*, preceding paper in this issue.
(2) The low solubility of tyrosine in $H_2O$ precluded its study directly. Typically, saturated solutions of the amino acids in water (2 mL) were stirred at 0 °C for 2 min with 1 mL of $CDCl_3$ containing ca. 0.5 mg of **1**. The organic phase was dried ($Na_2SO_4$) and concentrated to record the NMR spectrum. The amino acids were readily washed out of such samples by mere shaking with water.
(3) For a recent discussion, concerning the hydrophilicities of amino acid side chains, see: Wolfenden, R.; Anderson, L.; Cullis, P. M.; Southgate, C. C. *Biochemistry* **1981**, *20*, 849-855.
(4) Rebek, J.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.*, in press.
(5) Lehn, J. m. *J. Chem. Soc.* **1973**, *95*, 6108-6110. Newcomb, M.; Toner, J. L.; Helgeson, C.; Cram, D. J. *Ibid.* **1979**, *101*, 4941-4947.
(6) Pederson, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036. For a more recent study, see: Behr, J.-P.; Lehn, J.-M.; Vierling, P. *Helv. Chim. Acta* **1982**, *65*, 1853-1866.

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