clusters by low kinetic barriers. Further studies of the properties and reactivity of this complex are in progress.

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Supplementary Material Available: Details of the structure refinement and tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates (3 pages); table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Chiral Recognition of Aromatic Carboxylate Anions by an Optically Active Abiotic Receptor Containing a Rigid Guanidinium Binding Subunit

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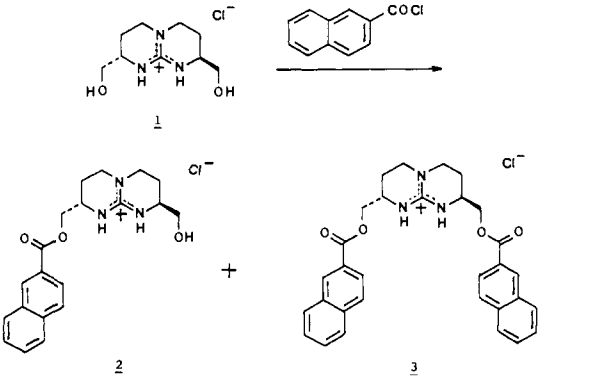
Molecular recognition by abiotic synthetic receptors is an important goal in current bioorganic chemistry. To achieve selectivity, a number of recognition features (i.e., electrostatic or hydrophobic interactions, hydrogen bonds) must be incorporated to the molecular receptor to complement, in a multiple point binding, the chemical characteristics of the substrate.[2] For anionic substrates, positively charged or electron-deficient binding sites are required.[3] This may be accomplished either by Lewis acid-containing receptors,[4] by ammonium quaternary salts,[5] or by protonated polyamines[6] and guanidines.[7] The guanidinium group (pk_a ca. 13.5) remains protonated over a much wider range of pH than does the ammonium group and forms characteristic pairs of well-organized, strong zwitterionic hydrogen bonds (N–H$^+$···O$^-$) with carboxylates or phosphates. Nature offers a number of examples of this bonding pattern, involving the arginine side chains of proteins.[8]

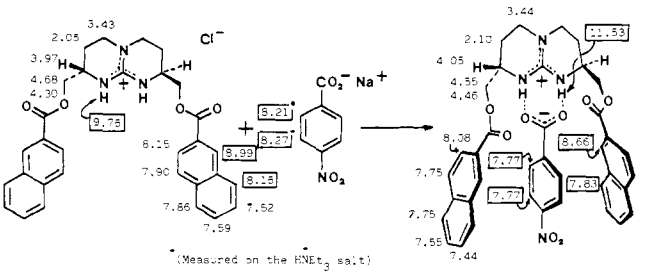
We recently described the synthesis of the rigid bicyclic guanidine subunit **1**, which was assembled in nine steps from asparagine. Both enantiomers **1**-*SS* and **1**-*RR* were obtained in excellent optical purity from L- and D-asparagine, respectively.[9] We present herein evidence for the complexation of aromatic carboxylic oxoanions by a bis-naphthoyl derivative of **1** and the first example of chiral recognition of anions, namely the enantiomers of the sodium salt of *N*-acetyltryptophan.

Reaction of **1** with 2-naphthoyl chloride (3 equiv) in dry *N*,*N*-dimethylformamide with an excess of triethylamine afforded a mixture of the mono- and bis-naphthoyl esters, **2** and **3**, in 20% and 58% yields, respectively (eq 1).[10]



(1)

Sodium *p*-nitrobenzoate was quantitatively extracted from water by a chloroform solution of **3**. Despite its ionic structure, no traces of **3** were found in the water layer, and the chloroform extract was composed exclusively by the *p*-nitrobenzoate guanidinium salt (eq 2). The ^{1}H NMR spectrum revealed significant shifts for



(2)

most signals of both ions in the 1:1 complex. For instance, NH guanidinium protons showed a 1.78 ppm downfield shift relative to **3**, whereas most aromatic protons of the host and the guest shifted upfield. Moreover, both multiplets corresponding to the methylene protons of the host side arms approached each other from 0.40 to 0.09 ppm apart. These data strongly support formation of a complex of a well-defined geometry, involving a double recognition of the guest by the guanidinium cation (zwitterionic hydrogen bonds with the carboxylate function) and the naphthoyl

(1) (a) Instituto de Química Orgánica, CSIC. (b) Universidad Autónoma de Madrid. (c) Université Louis Pasteur.

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(10) Both compounds were separated by flash silica gel chromatography (15:1 dichloromethane–methanol) and fully characterized by combustion analysis and ^{1}H and ^{13}C NMR spectroscopy. Data for **3**: mp 206–207 °C; $[\alpha]^{20}_D$ = +123.0° and −117.4° for the (*SS*) and (*RR*) enantiomers, respectively (c = 0.5, $CHCl_3$).

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side arms (stacking with *p*-nitrophenyl moiety). The stability constant K_s = 1609 M^{-1} (±12%) was determined by NMR titration of **3** in $CDCl_3$ with triethylammonium *p*-nitrobenzoate.[11,12]

Similarly, sodium *p*-methoxybenzoate and sodium phenylacetate were extracted by **3**, and NH guanidinium protons shifted downfield, whereas aromatic naphthoyl protons shifted upfield. However, the overall effect was somewhat lower than in the *p*-nitrobenzoate case. For example, the naphthoyl H_1 proton shifted only 0.27 and 0.26 ppm in the *p*-methoxybenzoate and the phenylacetate complexes, respectively.

The chirality of **3** should force any substrate to bind in a dissymetric environment, allowing the enantioselective recognition of chiral carboxylic acids. Extraction experiments of sodium (*S*)-mandelate and (*S*)-naproxenate [(+)-6-methoxy-α-methyl-2-naphthaleneacetate] with both enantiomers **3**-*SS* and **3**-*RR* afforded the corresponding diastereomeric salts. Chemical shifts for these complexes were quite similar as those for the achiral guests mentioned above, but small differences in both diastereomeric salts of each guest were observed. For instance, the naphthoyl H_1 protons of the **3**-*SS* host showed upfield shifts of 0.26 (mandelate) and 0.27 ppm (naproxenate), but the shifts were 0.30 and 0.32 ppm, respectively, when the **3**-*RR* host was employed. It was also noteworthy that in the naproxen complexes, the proton at the chiral carbon center of guest shifted upfield quite differently in both species: 0.11 ppm for the **3**-*SS* host but only 0.05 for the **3**-*RR* one.[13]

Free amino acids in zwitterionic form (i.e., valine, phenylalanine, tryptophan) were not extracted from aqueous solutions by **3**, hence *N*-acetyl and *N*-*tert*-butoxycarbonyl derivatives of sodium tryptophan were examined, since they contained two recognition functions (the carboxylate and the well-known π-donor indole ring) and a bulk substituent to interact sterically with the host aromatic side arm not involved in the stacking. Indeed, extraction of an excess of the racemic salts with **3**-*SS* afforded two diastereomeric salts in each case, with diastereomeric excesses (de) of ca. 17% for the L-tryptophan derivative.[14] For the *N*-acetyl derivative, a 1.07 ppm downfield shift was observed for the guanidinium NH protons, whereas naphthoyl protons shifted upfield (0.22 ppm for H_1). Both diastereomeric complexes became evident from the well-differentiated downfield shifted signals of the guest: NH (0.16 and 0.19 ppm) and methyl (0.21 and 0.32 ppm). NMR titration of the triethylammonium salts of *N*-acetyltryptophan in $CDCl_3$ gave K_s = 1051 (±19.3%) and 534 (±15.6%) M^{-1} for the L- and D-enantiomers, respectively. A similar de was obtained when the sodium salt of D-*N*-acetyltryptophan was extracted with the enantiomeric receptor, **3**-*RR*. This represents, to our knowledge, the first example of enantioselective recognition of anionic species by an abiotic receptor. Studies toward the design of more selective receptors, based on three-point binding hosts (derived from **2**), are underway.

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Supplementary Material Available: NMR spectroscopic data for **3** and its complexes (6 pages). Ordering information is given on any current masthead page.

(11) To minimize standard deviations, three independent titrations at different constant host concentrations (ranging from 6×10^{-3} M to 4×10^{-2} M) were carried out at 20 ± 1 °C. Typical saturation curves for 1:1 complexes were observed by measuring shifts on the naphthoyl H_1 signal. Curve fitting was performed with a modified version of program SALS (Statistical Analysis with Least Squares Fitting) programmed by T. Nakagawa and H. Togawa at the University of Tokyo, Japan.

(12) Due to the presence of chloride and triethylammonium ions in the solution, changes in the NMR spectra of this 1:1 mixture were lower than those observed in the extraction experiment. Chemical shifts were also found to be strongly dependent on the nature of the counterions. For example, a very large downfield shift (3.24 ppm) was observed for the guanidyl protons in the 1:1 mixture of the Ph_4B^- salt of **3** and Bu_4N^+ *p*-nitrobenzoate. Therefore, stability constants for these ion pairs could be influenced by the nature of the counterions or by the presence of other salts in the solution.

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(14) Diastereomeric excess was determined by NMR integration from the areas of the acetyl or the *tert*-butyl signals. A 1:4 CD_3OD–$CDCl_3$ solution was employed to achieve a better separation of the signals.

Synthesis and Structure of the First Example of a Four-Electron Donor, Side-On Bridging Thiocarbonyl Ligand

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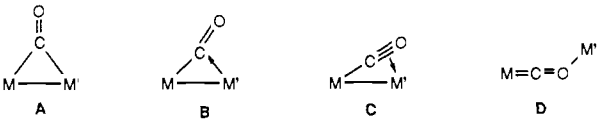
The similarity of carbon monosulfide (CS) to CO has stimulated much interest in the synthesis and reactivity of CS complexes.[1] There are four types of CO bridging ligand:[2] carbon bridging (A), semibridging (B), in which a filled orbital on M′ donates into



the empty π* orbital of the CO ligand, side-on bonding (C), involving donation from the filled π-orbital of the CO ligand into an empty orbital on M′, and end-on (D). Unlike CO, CS has not been found or suggested to be a side-on bridging ligand (type C) in any metal complexes. The C–S group is known as a carbon-bridging ligand (e.g., $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$,[3] $MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2Cp)$,[4] as an end-to-end bridging ligand (e.g., $(dppe)_2(CO)W{-}C{\equiv}S{-}W(CO)_5$,[5] $(\eta^6\text{-}C_6H_5Me)(CO)_2Cr{-}C{\equiv}S{-}Cr(CO)_5$),[6] and as a semibridging ligand (e.g., $[HB(pz)_3](CO)W(\mu\text{-}CO)(\mu\text{-}CS)Au(PR_3)$, R = Me, Ph).[7] In all of these types of complexes, the CS ligand has a greater preference for the bridging position than CO. In this communication, we describe the synthesis and structure of $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2(In)$ (**1**; In = $\eta^5\text{-}C_9H_7^-$, indenyl; $HB(pz)_3^-$, hydrotris(1-pyrazolyl)borate), the first example of a complex containing a side-on bridging CS ligand. In this type of bridging situation, the CS ligand also forms a more stable complex than CO.

Addition of 1 equiv of $[(In)Mo(CO)_2(MeCN)_2]BF_4$[8] to a THF solution of $Bu_4N\{[HB(pz)_3](CO)_2W(CS)\}$[9] (0.553 mmol) at 25 °C produces a brown solution of **1** in 30 min. After the solvent is removed in vacuo, the resulting brown residue is recrystallized several times from THF/Et_2O. A final recrystallization from

† Iowa State Molecular Structure Lab.

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