Molecular Recognition: The Demonstration of 1,3-Bis[(pyrid-2-ylamino)carbonyl]adamantane as an Exceptionally Versatile Assembler of One-Dimensional Motifs

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Abstract: Syntheses and crystal structures of 1,3-bis[(pyrid-2-ylamino)carbonyl]adamantane (**1**) and its perchlorate salt, copper(II) complex, and 1:1 complexes with a large variety of simple and functionalized 1,ω-alkanedicarboxylic acids, HOOC−X−COOH [X = $(CH_2)_n$, n = 2, 3, 5, and 8; −CH_2−CO (α-ketoglutaric acid); CH=CH (maleic acid)] are described. The molecule **1** exhibits remarkable adaptability with respect to the conformation of its two hydrogen-bonding subunits to suit the requirements of the assembling partners so as to generate persistently one-dimensional motifs, for example, infinite zig-zag ribbons with perchlorate ions and chains with both Cu(II) ions and dicarboxylic acids.

Introduction

In recent years, considerable interest has been shown in the study of molecular self-assemblies[1] both from a mechanistic as well as application perspective. Design of molecules that can direct the self-assembly of other neutral molecules or ions into preordained motifs by noncovalent interactions is an area of current interest,[2] particularly in the context of generating new molecular materials. In recent years, several approaches toward this objective have been reported.[1] One popular approach has been to incorporate into the molecule a small number of functional groups that can interact intermolecularly and to use these interactions to limit the possible orientations of the molecule in space with respect to one another. The most attractive types of functional groups for general use in controlling intermolecular orientations in crystals now seem to be those that can participate in hydrogen bonding. Of all the known hydrogen-bonding groups, the amide group is recognized as the most promising functionality to use in designing extended self-assemblies with reasonably predictable hydrogen-bonding patterns.[3ab] The hydrogen-bonding motif adopted by an amide group depends upon several factors, the most important being the steric constraint. Thus, while acyclic amides form largely chain motifs, the cyclic amides often restrict the amide group to the cis conformation, promoting two-point interactions leading to highly ordered hydrogen-bonded tapes, ribbons, and sheets or layer motifs.

Bisamides having the two amide groups separated by a rigid linker are good candidates for forming linear aggregates of tapes and ribbons. Incorporation of an additional hydrogen-bond donor or acceptor to form a complementary hydrogen-bonding pocket for a particular functional group in the molecule of interest imparts receptor properties to bisamides. This strategy has recently been used in the design of bis-pyridylamides with appropriate aromatic spacers as receptors for dicarboxylic acids.[4]

In search for a conformationally and geometrically well-defined rigid linker that can orient the bisamide subunits to

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(3) (a) Etter, M. C.; Reutzel, S. M. *J. Am. Chem. Soc.* **1991**, *113*, 2586. Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. Etter, M. C.; Lipkowska, Z. U.; Ebrahini, M. Z.; Panunto, T. W. *J. Am. Chem. Soc.* **1990**, *112*, 8415. (b) Another hydrogen bonding functionality that is gaining increasing importance in supramolecular chemistry is the carboxylic group (Rebek, J., Jr., Nemeth, D.; Ballester, P.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 3474. Nowick, J. S.; Ballester, P.; Ebmeyer, F. Rebek, J. Jr., *J. Am. Chem. Soc.* **1990**, *112*, 8902. Chang, Y.-L.; West, M. A.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5991. Yang, J.; Marendaz, J.-L.; Geib, S. J.; Hamilton, A. D. *Tetrahedron Lett.* **1994**, *35*, 3665. Also see ref 1).

(4) The promise of the 2-aminopyridine group as a −COOH binding pocket was first demonstrated by Etter et al. (Etter, M. C.; Adsmond, D. A. *J. Chem. Soc., Chem. Commun.* **1990**, 589) in the formation of hydrogen-bonded infinite ribbons in 1:1 molecular complex of 2-aminopyrimidine and succinic acid. Subsequently, this unit has been extensively used by Hamilton and co-workers (Garcia-Tellado.; Geib, S. J.; Goswami, S.; Hamilton, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 9265) in the design of dicarboxylic acid receptors by a common strategy that involved linking the two aminopyridine groups through a rigid aromatic spacer. A variety of aromatic spacers ranging from simple phenyl to more complex, naphthyl, biphenyl, and terphenyl units were used to create cavities of different sizes for accommodating dicarboxylic acids of varied lengths. In cases where the length of the dicarboxylic acid did not correspond to the cavity size, an alternate mode of binding was observed in the form of infinite ribbons, with each receptor molecule binding to two different molecules of dicarboxylic acid, one above and the other below the cavity resulting in extended structures (Geib, S. J.; Vincent, C.; Fan, E.; Hamilton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 119).
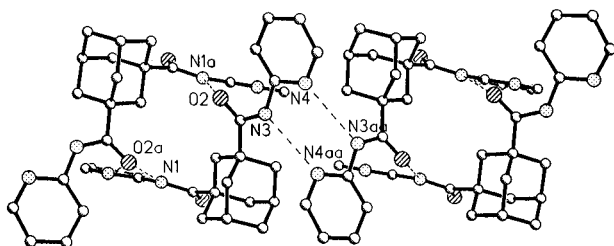
Figure 1. Dimeric structure of **1** in the solid state. The dimers are linked into an infinite ribbon by pairs of N3H···N4 hydrogen bonds that are relatively weak (N···N 3.29 Å, H−N 2.38 Å).

create self-assemblies, with compatible partners, in persistently one-dimensional motifs, we opted for the 1,3-adamantane dicarbonyl unit, a particularly appealing structural framework containing four chair forms of cyclohexane with all the bridgehead hydrogen atoms in equatorial disposition with respect to each of the rings, and wherein the hydrogen-bonding pockets would be tetrahedrally disposed, particularly suited for creating infinite linear arrays.

In this paper, we introduce 1,3-bis[(pyrid-2-ylamino)carbonyl]-adamantane (**1**) as a novel assembler molecule that shows a unique property of self-assembly with perchlorate ions into infinite hydrogen-bonded zig-zag ribbons, with Cu(II) ions into highly organized polynuclear linear arrays, with 1,ω-alkane dicarboxylic acids into infinite chains and the molecule itself assembles, in the uncomplexed form, into hydrogen-bonded cyclic dimers.

Results and Discussion

The bisamide **1** endowed with four hydrogen-bond acceptors (an equivalent pair, each, of pyridyl nitrogens and amide oxygens) and two hydrogen-bond donors (an equivalent pair of amide NHs), has the advantage of creating six hydrogen-bonding interactions. We envisaged that the adamantyl spacer in **1** would introduce more demanding spatial requirements between the 1,3-bis(pyridylamino) subunits. Consequently, the two terminal hydrogen-bonding pockets would be forced to adopt a syn-anti conformation, an arrangement most suitable for generating continuous self-assemblies in preference to discrete complexes with complementary hydrogen-bonding partners.

The 1,3-bis[(pyrid-2-ylamino)carbonyl]adamantane (**1**) was readily synthesized in near-quantitative yields from 1,3-ada-mantanedicarbonyl chloride and 2-aminopyridine. The broad signals observed for the proton resonances in the ^{1}H NMR spectrum indicated that in CDCl$_3$ solution **1** was present as a mixture of all three possible conformers (syn-syn, syn-anti, and anti-anti)[5] arising as a result of free rotation about the adaman-tyl−CO bond.

Interestingly, in the solid state, the adamantyl spacer as anticipated restricts the conformation of the 1,3-bis(pyridylamino)subunits to a syn-anti arrangement. The bisamide **1** in this conformation is self-complementary and dimerizes to form cyclic dimers (Figure 1) through a symmetrical pair of N−H···O (N···O 3.05, H···O 2.16 Å) hydrogen bonds. The 16-membered centrosymmetric dimer has a cavity size of 4.36 × 3.74 Å (distances O2−O2a = 4.36 Å; C2−C2a = 3.74 Å).

The presence of two 2-aminopyridine subunits, the well-established carboxylic acid binding pockets,[3,4] and their syn-anti relationship in bisamide **1** suggested that the adamantyl-partitioned bisamide **1** may be tailor-made for creating infinite hydrogen-bonding linear arrays of 1,ω-dicarboxylic acids.[4]

The bisamide **1** was treated with a range of 1,ω-dicarboxylic acids (a) with the general formula HOOC−(CH$_2$)$_n$−COOH (n = 0, 1−8, and 20), (b) maleic and fumaric acids, (c) core-modified retro-bispeptide acids HO-Leu-X-Leu-OH (X = COCO or CO(CH$_2$)$_2$CO), and (d) α-ketoglutaric acid (an important intermediate in Kreb's cycle) in equimolar proportions in THF. The complexes were crystallized from chloroform solution by slow diffusion of hexane vapor. In each case, formation of a 1:1 hydrogen-bonded complex was indicated in the ^{1}H NMR by appearance of new resonances in the 1.5−2.5 ppm region (due to the CH$_2$s of dicarboxylic acids), the large downfield (1.3−1.5 ppm) shift of the amide NH resonances of **1**, and integration of the ^{1}H NMR spectra (Supporting Information).

The FT-IR spectra of all the dicarboxylic acid complexes reported here[6] displayed two equally intense broad bands near 1900 and 2500 cm^{-1}. These low frequency bands have been interpreted as characteristic of a carboxylic acid hydrogen bonded to an aromatic ring nitrogen.[7] Further, these complexes exhibited similar characteristics as their parent dicarboxylic acids in the $\nu_{C=O}$ and ν_{C-O} region of the spectra, which indicates that the state of the complex is AH···B rather than A$^-$-BH$^+$. In these complexes, the $\nu_{C=O}$ frequency was equal to or higher than that of the parent acid. The neutral character of the dicarboxylic acid complexes was further supported by comparison of their FT-IR spectra (Supporting Information) with the perchlorate salt of **1**, which showed absence of low frequency ν_{-OH} bands. The characteristic low-frequency ν_{-OH} bands near 2500 and 1900 cm^{-1} were also seen in the solution (CHCl$_3$) spectra of the dicarboxylic acid complexes (Supporting Information), indicating that the complexes retain their hydrogen-bonded character in solution.

Further, the ROESY NMR spectra of glutaric and pimelic complexes of **1** (Supporting Information) showed complete absence of cross peaks between the β- and γ-CH$_2$ resonances of the dicarboxylic acids with the pyridine protons. Cooling the CHCl$_3$ solution from 298 to 233 K did not change the chemical shifts of the dicarboxylic acid β- and γ-CH$_2$ resonances. These observations indicated an extended nature of the complexes.[4]

(5) The syn-syn, syn-anti, and anti-anti terms refer, respectively, to the conformation with the 2-aminopyridine subunits pointing into the center, one inside and the other outside, and both outside the cavity.

(6) The only exception was the maleic acid complex, which showed very weak ν_{-OH} low-frequency bands in its FT-IR. This observation augurs well with the ΔpK_a value of ∼5 between the acid and aminopyridine, indicative of the possibility of a partial proton transfer from the carboxylic −OH group.
(7) Johnson, S. L.; Rumon, K. A. *J. Phys. Chem.* **1965**, *69*, 74.
(8) The conclusions derived from FT-IR data were correlated with ΔpK_a values. A value of ≥3 for the ΔpK_a between an acid and a protonated pyridine has been estimated for the formation of an ionic complex in preference to a neutral hydrogen-bonded species.[7] The pK_1 values [dicarboxylic acid pK values (pK_1, pK_2): maleic (1.83, 6.07); succinic (4.16, 5.61); glutaric (4.34, 5.41); adipic (4.43, 5.41); pimelic (4.71); suberic (4.52): *CRC Handbook of chemistry and physics*, 66th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL; 1985] for the dicarboxylic acids in the present study fall in the range of 4−5 and the calculated value for pK_a of 2-aminopyridinium ion is 6.82, thus maintaining ΔpK for the complexes to an optimum value of <3, well suited to form hydrogen-bonded nonionic complexes.[7] This is reflected in the appearance of two distinct ν_{-OH} bands in the 1900−2500 cm^{-1} region. With an increase in ΔpK_a values (>4), a proton transfer takes place that results in the sharpening of the ν_{-NH} band and the disappearance of ν_{-OH} low-frequency bands. The complex of **1** with perchloric acid (the strongest mineral acid known with pK_a −10) shows the expected FT-IR characteristic of an ionic complex (Supporting Information).
(9) Although the solid-state structure of the maleic acid complex of **1** indicates that the acidic proton is preferably localized on the carboxylic oxygen in preference to the pyridyl nitrogen (O···H, 0.93, 1.01 Å; pyr N···H, 1.58, 1.69 Å), the evidence based on ΔpK_a (4.99) criteria and FT-IR (very weak low frequency ν_{-OH} bands) studies supports at least a partial proton transfer.
(10) The bisamide **1** was also shown to form 1:2 complexes, similar to maleic acid, with monocarboxylic acids such as crotonic, phenylacetic acid, and prostaglandin E$_1$. Although the complex formation in these cases was established by ^{1}H NMR in CDCl$_3$ (spectra located in the Supporting Information), all attempts to crystallize them resulted in isolation of individual components.
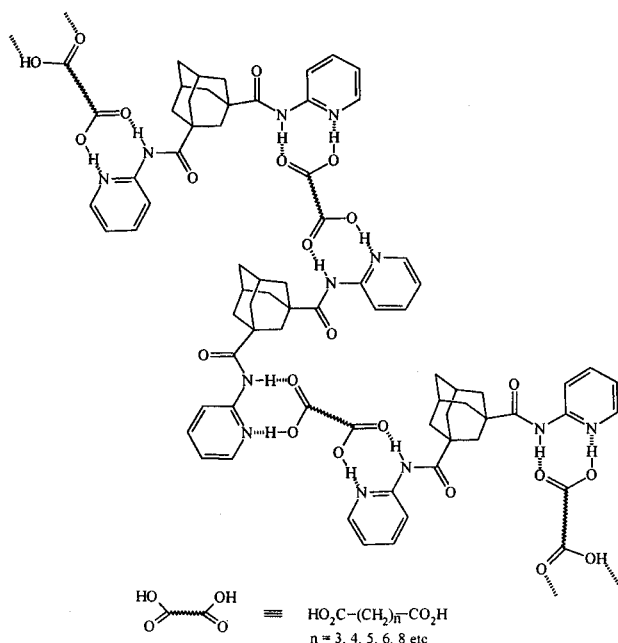
Figure 2. Schematic representation of the infinite chain assembly of **1** with dicarboxylic acids.

X-ray quality crystals were obtained in complexes of **1** with maleic, succinic, glutaric, α-ketoglutaric, pimelic, and sebacic acids. Crystal structures of these complexes provided proof for the recognition interactions and showed that in all cases except succinic acid complex the bisamide **1** retains its syn-anti conformation and the dicarboxylic acid displays one trans and one gauche conformation (about its CH_2-CH_2 bonds). Such an arrangement of the components is ideally suited to result in binding of the bisamide **1** to two different dicarboxylic acid molecules, one below and other above the plane of the cavity through bidentate hydrogen bonding of the 2-aminopyridine unit with the −COOH function. The self-assembly pattern in the crystal structure of 1:1 complex of **1** with $HOOC-(CH_2)_n-$ COOH ($n = 3, 5, 8$) and with α-ketoglutaric acid (presented in Figure 2 in schematic form) shows that complexation results in the formation of infinite chains with alternating components held together by a network of complementary hydrogen bonds.

Figure 3a−c shows, respectively, the self-assembly pattern of 1:1 complexes of **1** with glutaric ($n = 3$), pimelic ($n = 5$), and sebacic ($n = 8$) acid in the solid state. The persistent formation of a chain motif in the dicarboxylic acid assembly was further supported by the crystal structure (Figure 3d) of a 1:1 complex of **1** with the metabolically important α-ketoglutaric acid. The four hydrogen bonds between aminopyridine units and dicarboxylic acid seen in the repeating unit of above complexes fall in the range of ∼3 Å (amide N⋯O) and ∼2.7 Å (pyridine N⋯O). Examination of the hydrogen-bond distances in the above complexes suggests that although the carboxyl O⋯H distance in these adducts is slightly larger than the normal value, it may still be concluded that the acidic proton is preferably localized on the carboxylic oxygen (O⋯H, 0.9− 1.1 Å; Pyr N⋯H, 1.58−1.75 Å), thus supporting the conclusions reached in FT-IR studies that no proton transfer to form a carboxylate−pyridinium ion pair has occurred. It may be noted that in the perchlorate salt of **1** where complete proton transfer had occurred the O⋯H and Pyr⋯H distances were found to be 2.34 and 0.90 Å, respectively. Table 1 presents the detailed hydrogen-bonding parameters.

The importance of the methylene spacer in the control of self-assembly was highlighted in the crystal structure of the 1:1 complex of **1** with succinic acid ($n = 2$). The switch-over from syn-anti to anti-anti conformation of the binding pockets of **1**

in the presence of succinic acid forces the bisamide to assemble succinic acid molecules in a discrete [2 + 2] cyclic aggregate held together by eight N−H⋯O bonds, as part of four nine-membered hydrogen-bonded rings in a large macrocycle (Figure 4a). The succinic acid molecule displays an all-trans conformation in the complex. Maleic acid, an olefinic (Z) diacid, forms a 2:1 complex with **1**. This is because the dicarboxylic acid is internally folded into a seven-membered hydrogen-bonded ring (O⋯O ∼2.5; H⋯O ∼1.40 Å) essentially behaving as a monocarboxylic acid[9,10] (Figure 4b).

The presence of pyridyl ring nitrogens in **1** offered an exciting possibility of exploring the formation of proton-transfer-triggered self-assemblies of **1** with strong acids. This was initially tested with perchloric acid, one of the strongest mineral acids (pK_a = −10) known. The perchlorate salt of **1** (obtained in quantitative yields by admixing an acetonitrile solution of **1** with $HClO_4$ in 1:2 molar ratio; mp 306−308 °C) revealed in its X-ray crystal structure a preference for cis-cis (cofacial) orientation of the two sets of N, O coordinating centers. The crystal structure further showed that a complete proton transfer had taken place from perchloric acid, and the protonated pyridyl N participates in bifurcated hydrogen bonding with adamantyl carbonyl (N⋯O 2.60, H⋯O 1.91 Å) on one hand and with perchlorate oxygen (N⋯O 2.99, H⋯O 2.34 Å) on the other, creating a six-membered hydrogen-bonded ring on either side of the spacer, which further stabilizes the cis-cis conformation of the bidentate pockets. Two such units are cross-linked by four perchlorate ions, symmetrically placed in pairs. All the hydrogen-bonding donors and acceptors in **1** are utilized in this arrangement, which extends into infinite zig-zag ribbons. Figure 5a−c shows, respectively, the X-ray structure, the schematic representation, and the edge-on view of the perchlorate assembly in the solid state. A noteworthy feature of this unprecedented and extremely ordered self-assembly is the involvement of the perchlorate ion as a bidentate bridge in hydrogen-bonding network.[11]

The cofacial orientation of N, O coordinating sets in **1** appeared ideally poised for creating infinite self-assembly of Cu(II) ions.[12] This was demonstrated in the Cu(II) complex[13] (obtained as brilliant blue crystals in quantitative yields by mixing acetonitrile solution of **1** and $Cu(ClO_4)_2\cdot6H_2O$ in 1:1 molar proportions) whose X-ray structure revealed a unique, one-dimensional polynuclear assembly of Cu(II) ions as infinite linear arrays wherein each Cu(II) center is bonded to two different molecules of the ligand in a five-coordination mode.

(11) The ClO_4^- ion, a hard base, does not normally coordinate or participate in hydrogen bonding. However, when no other donor is present to compete, the perchlorate ion exercises a donor capacity and can be monodentate, bridging bidentate, or chelating bidentate (Potier, J. *Inorg. Chem.* **1985**, *24*, 238). To our knowledge, the present finding represents the first example of a hydrogen-bonding self-assembly of perchlorate ions.

(12) In order to be able to promote the formation of a self-assembly, the ligand should not use up all its coordination sites in binding to a single metal center (Carina, R. F.; Bernardinelli, G.; Williams, A. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1463). This concept was recently exploited by us (Ranganathan, D.; Vaish, N. K.; Chandramouli, G. V. R.; Varghese, B.; Muthukumaran, R. B.; Manoharan, P. T. *J. Am. Chem. Soc.* **1995**, *117*, 1643) in the creation of an infinite two-dimensional layered self-assembly of (Aib-CO-CO-Aib)Cu$_2$ modules. The rigid adamantane spacer in the bisamide ligand **1** appeared as a judicious choice to achieve this objective. Thus, the preference of Cu(II) ion for a four-coordinate square-planar geometry and the rigidity of the 1,3 adamantyl spacer forcing the ligand to act as a bis-bidentate rather than a tetradentate appear to be the most likely driving factors for the formation of an infinite assembly.

(13) The copper complex (mp 270 °C dec) showed a characteristic axial EPR spectrum (solid, room temp, $g_{\parallel}$ = 2.278; $g_{\perp}$ = 2.066; $A_{\parallel}$ = 150 G) typical of a square-pyramidal Cu(II) complex (Wei, N.; Murphy, N. N.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 6093). The UV−vis absorption spectrum [DMF, λ_{nm} (ϵ, M^{-1} cm^{-1}, sh = shoulder: 730 (60), 415 sh(75), 326 sh (920), 277 (11 600)] was also in agreement with the five-coordinated Cu(II) geometry (Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1196. McLachlan, G. A.; Falton, G. D.; Martin, R. L.; Spiccia, L. *Inorg. Chem.* **1995**, *34*, 254).
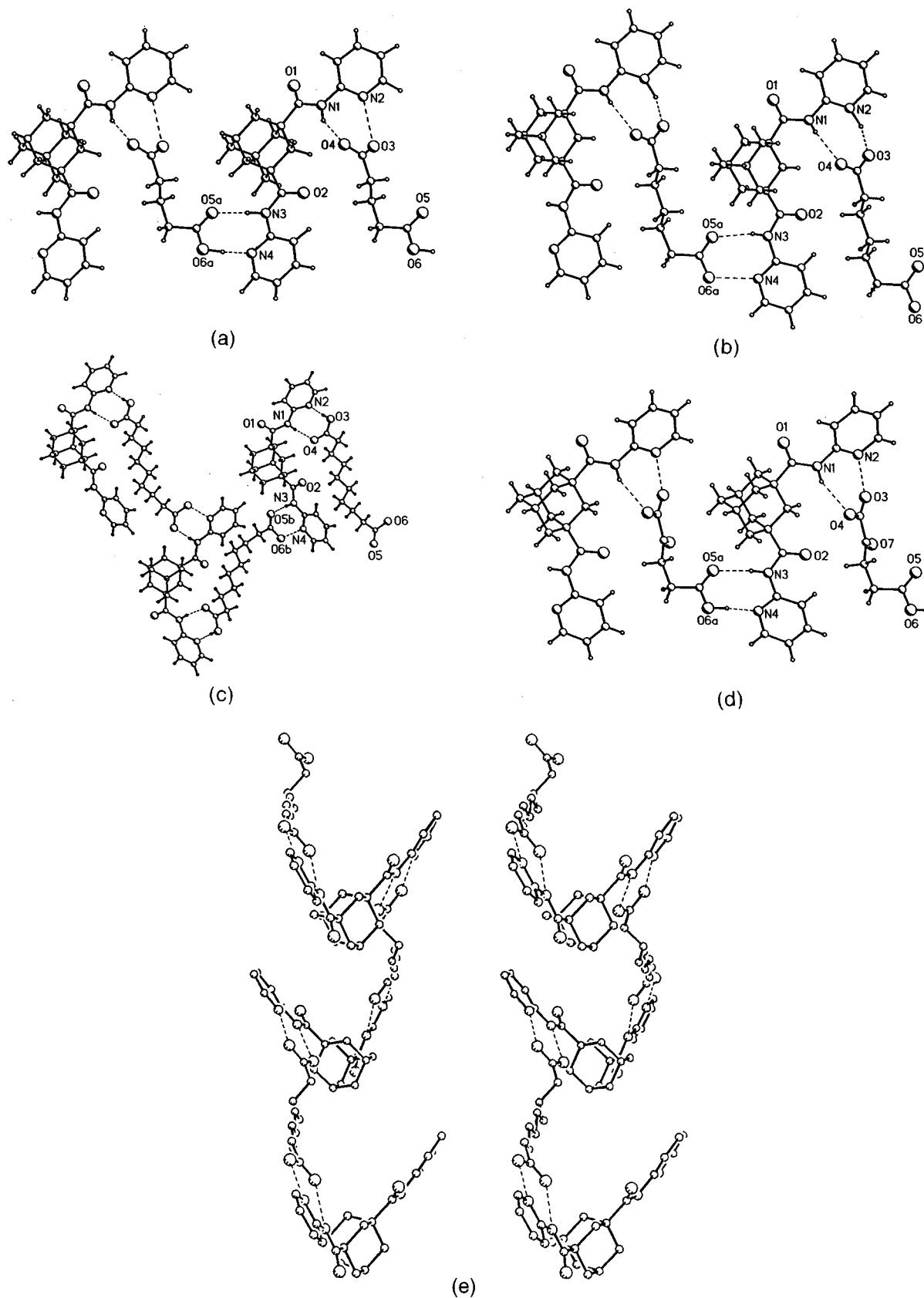
Figure 3. X-ray structure of the polymeric 1:1 complex of **1** with (a) glutaric (b) pimelic (c) sebacic, and (d) α-ketoglutaric acid. None of the individual molecules or complexes have internal symmetry. The repeat distance for each loop in the chain in a, b, and d is 11.2, 11.3, and 10.7 Å, respectively. The looped chains are relatively planar and pack in layers in their respective cells. Complexes in a, b, and d have a form similar to those shown in Figure 8 of the paper by Garcia-Tellado et al.[2k] The complex with the decanedicarboxylic acid in c has two loops in a repeat unit with a repeat distance of 16.6 Å. The looped chain in c is not planar, but forms a distorted helix around a 2-fold screw axis as shown in the stereodiagram in Figure 3e. Neighboring helices in c are intercalated (not intertwined).

The coordination to the Cu(II) center is provided by two molecules of **1**, each contributing a pair of nitrogen and oxygen donor sets resulting in an almost square-planar arrangement.

The fifth coordinating ligand is provided by a water molecule modifying the coordination geometry to a square pyramid with N and O atoms at the base and H_2O at the apex of the pyramid.

Table 1. Hydrogen Bond Parameters

complex of **1** with diacid	hydrogen bonds	N···O (Å) O···O (Å)	H···O (Å) H···N (Å)	∠NH···O (deg) ∠OH···O (deg)
maleic	N1H···O7a	3.023	2.19	169
	N2H···O8a	2.597	1.58	165
	N3H···O3a	2.960	2.02	170
	N4H···O4a	2.621	1.69	167
	O5aH···O3a	2.497	1.40	169
	O9aH···O7a	2.489	1.43	173
succinic	N1H···O4	3.069	2.30	162
	N2···HO3	2.658	1.65	146
	N3H···O5	3.003	2.30	167
	N4···HO6	2.688	*a*	*a*
glutaric	N1H···O4	3.196	2.34	150
	N2···HO3	2.727	*a*	
	N3H···O5	2.999	2.10	158
	N4···HO6	2.647	1.60	169
pimelic	N1H···O4	3.125	2.37	171
	N2···HO3	2.732	1.61	162
	N3H···O5	3.025	2.23	164
	N4···HO6	2.654	H between N4 and O6	
α-ketoglutaric	N1H···O4	3.076	2.34	141
	N2···HO3	2.583	H between N2 and O3	
	N3H···O5	2.928	2.03	169
	N4···HO6	2.676	1.67	173
sebacic	N1H···O4	2.974	2.08	172
	N2···HO3	2.675	1.75	168
	N3H···O5	2.977	2.08	175
	N4···HO6	2.615	H between N4 and O6	

a Hydrogen not found in electron density map.

The square-pyramid polyhedron[14] of the copper complex with relevant bond angles and bond distances[15] is presented in the Supporting Information.

This arrangement of bonding extends into an infinite poly-nuclear chain of Cu(II) ions with a Cu–Cu distance of 7.48 Å. Figure 6a–c shows, respectively, the X-ray structure, the schematic, and the cartoon representation of the Cu(II) chain assembly.[16]

Conclusion. In conclusion, the present study has shown that by judicious choice of a spacer unit it should be possible to design a receptor molecule that would preferentially form infinite vs discrete complexes. Use of a 1,3-adamantyl spacer in bisamide **1** has provided the desirable steric constraint forcing the two bidentate (2-aminopyridyl subunits) hydrogen-bonding pockets to adopt a syn-anti conformation in the presence of 1,ω-alkane dicarboxylic acids $(CH_2)_n(COOH)_2$ ($n \geq 3$), as demonstrated with the crystal structures of glutaric, α-ketoglu-taric, pimelic, and sebacic acid complexes, resulting in the formation of infinite chains of the alternating components, held

(14) The enzyme galactose oxidase provides a novel example of Cu(II) ion in a square-pyramidal coordination mode (Ito, N.; Phillips, S. E. V.; Stevens, C.; Ogel, Z. G.; McPherson, M. J.; Keen, J. N.; Yadav, K. D. S.; Knowles, P. F. *Nature* **1991**, *350*, 87).

(15) The Cu–O and Cu–N distances in the Cu(II) complex of **1** correspond well to the reported values in the known square-pyramidal complexes of Cu(II) (Hathaway, B. J. *Coord. Chem. Rev.* **1982**, *41*, 423–487. Pajunen, A.; Nasakkala, M. *Acta Crystallogr.* **1980**, *B36*, 1650. Pavelcik, F.; Majer, J. *Acta Crystallogr.* **1980**, *B36*, 1645).

(16) A unique feature of the chain assembly is the stabilization provided by the participation of the perchlorate ion in extensive hydrogen bonding. Two perchlorate ions are each bonded to the coordinated water ligand through a pair of O···H–O bonds [O···O 2.83, 2.81 Å] on one side of the Cu(II) polyhedron. On the opposite side, another water molecule provides a pair of hydrogen bonds to two perchlorate ions (O···O 3.10, 2.94 Å). The water molecule itself is bonded to the amide NH (N···O 2.91, H···O 2.03 Å). The ligand **1** has its second amide NH directly bonded to perchlorate ion (N···O 3.05, H···O 2.21 Å). A detailed picture showing hydrogen bonding of the Cu(II) complex to perchlorate ions and water molecules is given in the Supporting Information. In the third dimension, the infinite chains are connected through hydrogen bonds from water molecules W_1 and W_2 to perchlorate ions.
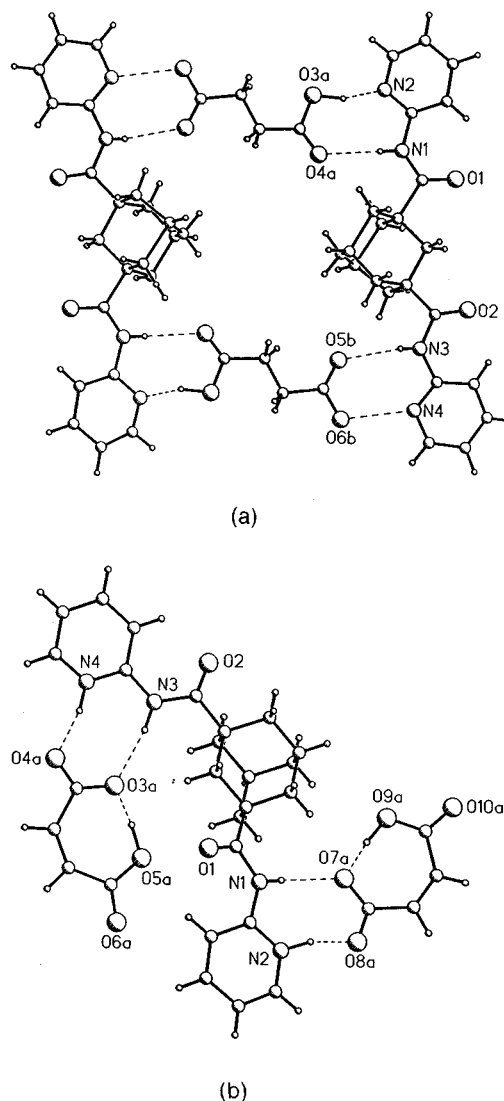

(a)

(b)

Figure 4. (a) [2 + 2] cyclic aggregate of **1** and succinic acid in solid state. The macrocycle is held together by eight hydrogen bonds (b) X-ray structure of 1:2 aggregate of **1** with maleic acid.

together by a network of complementary hydrogen bonds. With succinic acid ($n = 2$), the conformational switch to the anti-anti form in **1** leads to a discrete [2 + 2] assembly of a macrocycle held together by eight N–H···O bonds. Maleic acid, because of its internally hydrogen-bonded state, forms a 2:1 complex with **1** behaving like a monocarboxylic acid. The neutral character and stability of these complexes in solution was supported by ^{1}H NMR and FT-IR studies in chloroform. The bisamide **1** was also shown to form highly organized self-assemblies with ionic components. For example, the ligand **1** adopts a cofacial orientation of its two pairs of N, O coordinating centers in the presence of perchlorate and Cu(II) ions, resulting in the formation of highly organized hydrogen-bonded infinite ribbons with the former and unprecedented polynuclear chains with the latter partner.

The controlled assembly of ions and molecules in one dimension as demonstrated here with **1** is particularly important from the standpoint of crystal design and may have significance in the context of designing materials with special properties. The near-quantitative yields and stability of the dicarboxylic acid complexes both in solid as well as in solution provides additional incentive to design assembler molecules that may be useful as carriers for the selective transport of various types of substrates or as scavengers in purification or detoxification procedures.
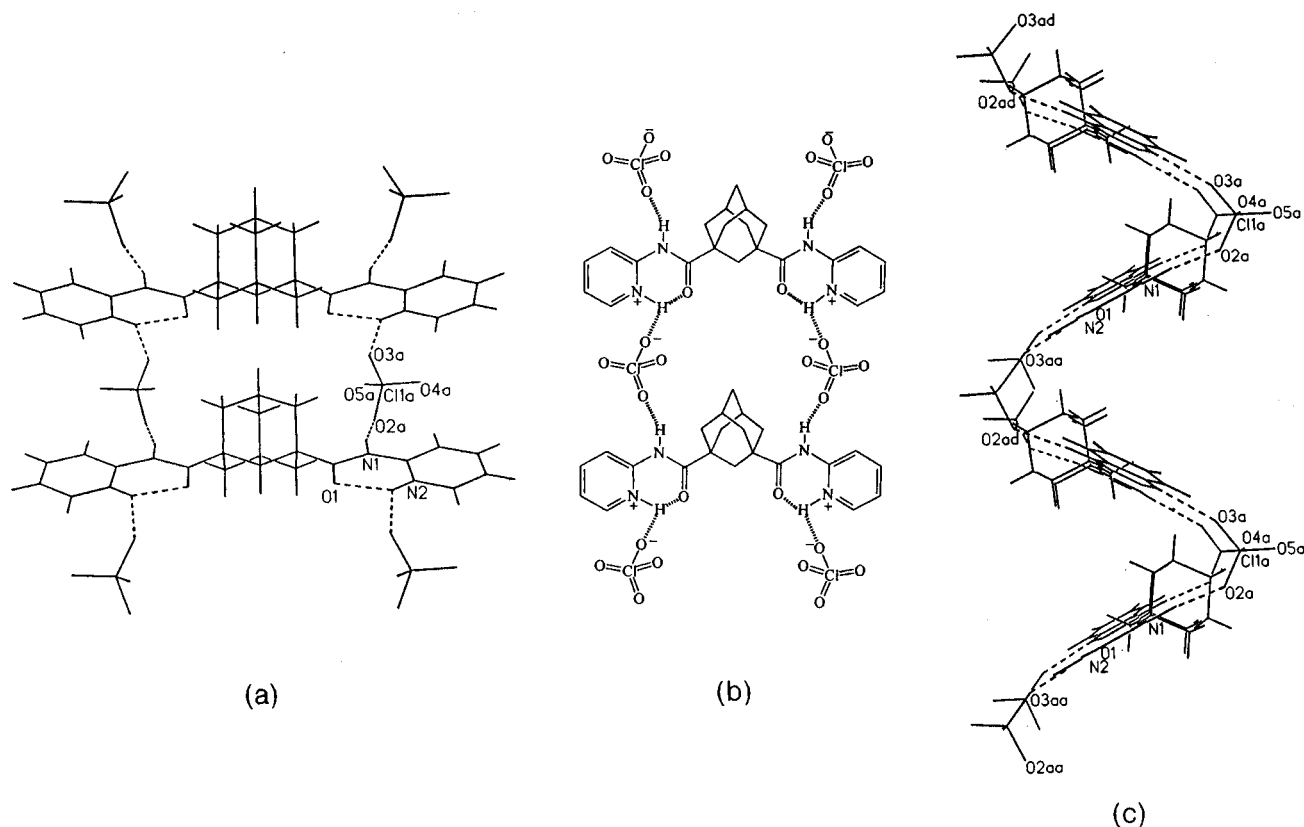
Figure 5. Hydrogen-bonded infinite ribbons of perchlorate salt: (a) X-ray structure, (b) schematic representation, and (c) an edge on view.
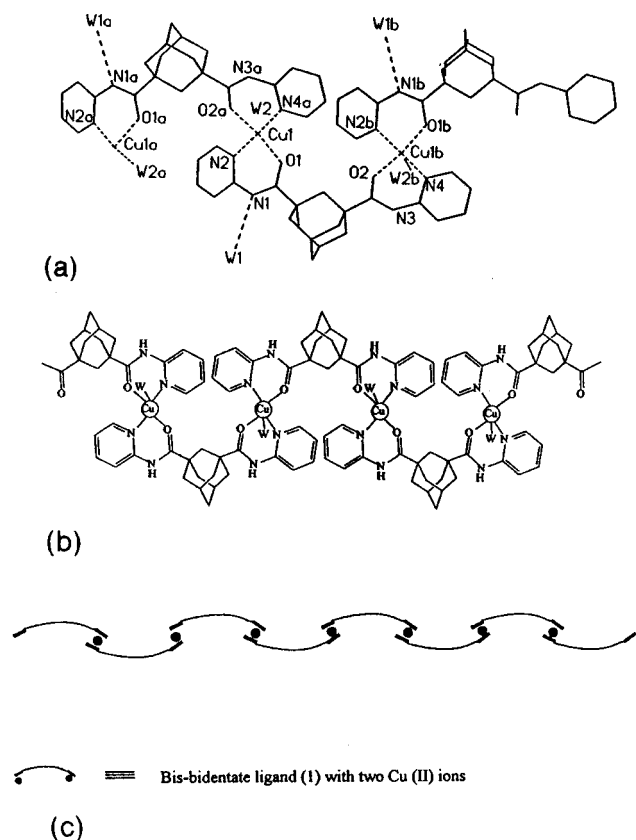

Figure 6. Infinite polynuclear strings of Cu(II) complex: (a) X-ray structure, (b) schematic representation, and (c) cartoon representation.

Experimental Section

Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer/1600FT spectrometer as KBr pellets, and prominent peaks are expressed in cm^{-1}. ^{1}H NMR spectra were recorded on a JEOL 90 MHz instrument. The chemical shifts are reported in δ ppm with TMS at 0.00 as an internal reference. FAB-MS were obtained on a JEOL SX-120/DA-6000 instrument using *m*-nitrobenzyl alcohol as the matrix. Electronic spectra of the copper complex were recorded on a Perkin-Elmer Lambda-2 UV−vis spectrophotometer at 298 K in DMF. Electron paramagnetic resonance (EPR) were recorded on a Varian E-109 spectrometer operating at the X-band using DPPH as the external standard.

1,3-Bis[(pyrid-2-ylamino)carbonyl]adamantane (1). A solution of freshly prepared 1,3-adamantane dicarbonyl chloride (1 mmol, prepared by refluxing 1,3 dicarboxylic acid with 3 M excess of SOCl$_2$) in dry CH$_2$Cl$_2$ was added dropwise to a well-stirred and ice-cooled solution of 2-aminopyridine and triethylamine (2.5 mmol each) in the same solvent. After 24 h of stirring at room temperature, the solvents were removed in vacuo and the residue was purified on a small column of silica gel using ethyl acetate and hexane as eluents to afford **1** in 95% yield: crystals from ethyl acetate/hexane; mp 173−175 °C; IR (KBr) 3292, 2920, 2860, 1665, 1595(sh), 1561, 1529, 1432 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.54−2.65 (m, 14H), 7.05 (t, 2H), 7.72 (t, 2H), 8.27 (m, 6H); (NH protons in DMSO-d_6) 9.50 (s, 2H, exchangeable); FAB-MS *m/z* 377 (100) (M + H)$^+$. Anal. Calcd for C$_{22}$H$_{24}$N$_4$O$_2$)$_2$: C, 70.19; H, 6.43; N, 14.88. Found: C, 69, 96; H, 6.40; N, 14.71.

Selected Data for Complexes of 1 with Dicarboxylic Acids. (a) Oxalic acid: ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.35−2.55 (14H, m), 7.10 (2H, m), 7.79 (2H, m), 8.35 (4H, m, 9.02 (2H, brs).

(b) Malonic acid: ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.55−2.48 (14H, m), 3.55 (2H, s), 7.09 (2H, m), 7.78 (2H,m), 8.25 (4H, m), 9.31 (2H, brs), 10.65 (2H, brs).

(c) Maleic acid: mp 124−126 °C; IR (KBr) 3426, 3198, 3075, 2937, 2864, 1713, 1690, 1640, 1575, 1552, 1524, 1435 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.53−2.48 (14H, m), 6.33 (4H, s), 7.25 (2H, m), 8.05 (4H, m), 8.44 (2H, m), 10.52 (2H, brs), 11.20 (4H, brs). Anal. Calcd for C$_{30}$H$_{32}$N$_4$O$_{10}$: C, 59.21; H, 5.30; N, 9.21. Found: C, 59.17; H, 4.83; N, 9.24.

(d) Succinic acid: mp 120−122 °C; IR (KBr) 3289, 2930, 2864, 2507, 1908, 1703, 1613, 1584, 1539, 1472, 1435 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.52−2.90 (18H, m), 7.05 (2H, m), 7.76 (2H, m), 8.22 (4H, m), 9.52 (2H, brs). Anal. Calcd for C$_{52}$H$_{60}$N$_8$O$_{12}$: C, 63.13; H, 6.12; N, 11.33. Found: C, 62.91; H, 5.82; N, 11.17.

(e) Glutaric acid: mp 125−127 °C; IR (KBr) 3285, 2936, 2863, 2513, 1925, 1693, 1611, 1584, 1532, 1476, 1436 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.62−2.60 (20H, m), 7.01 (2H, m), 7.73 (2H, m), 8.10 (2H, d, J = 5.0 Hz), 8.32 (2H, d, J = 5.0 Hz), 9.42 (2H, brs). Anal. Calcd for C$_{27}$H$_{32}$N$_4$O$_6$: C, 63.77; H, 6.34; N, 11.02. Found: C, 63.88; H, 6.02; N, 11.08.

(f) α-Ketoglutaric acid: mp 138−141 °C; IR (KBr) 3261, 2934, 2859, 2478, 1930, 1726, 1688, 1616(sh), 1585, 1523, 1438 cm^{-1}; ^{1}H NMR (90 (MHz, CDCl$_3$) δ 1.55−2.90 (18H, m), 7.08 (2H, m), 7.77 (2H, m), 8.10 (2H, d, J = 5.0 Hz), 8.36 (2H, d, J = 5.0 Hz), 9.50 (2H, brs), 9.90 (2H, brs).

(g) Adipic acid: mp 129−131 °C; IR (KBr) 3276, 2948, 2914, 2864, 2547, 1927, 1700, 1611, 1585, 1538, 1476, 1438 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.45−2.50 (22H, m), 7.00 (2H, m), 7.71 (2H, m), 8.23 (4H, m), 9.24 (2H, brs). Anal. Calcd for C$_{28}$H$_{34}$N$_4$O$_6$: C, 64.35; H, 6.56; N, 10.73. Found: C, 64.40; H, 6.52; N, 10.63.

(h) Pimelic acid: mp 128−130 °C; IR (KBr); 3284, 2924, 2864, 2535, 1929, 1697, 1688, 1611, 1584, 1534, 1471, 1439 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.31−2.50 (24H, m), 7.02 (2H, m), 7.72 (2H, m), 8.13 (2H, d, J = 5.0 Hz), 8.32 (2H, d, J = 5.0 Hz), 9.33 (2H, brs), 10.78 (2H, brs). Anal. Calcd for C$_{29}$H$_{36}$N$_4$O$_6$: C, 64.91; H, 6.76; N, 10.44. Found: C, 64.88; H, 6.73; N, 10.22.

(i) Suberic acid: mp 104−105 °C; IR (KBr) 3266, 2915, 2863, 2495, 1920, 1701, 1614, 1585, 1540, 1435 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.17−2.52 (26H, m), 7.02 (2H, m), 7.73 (2H, m), 8.18 (2H, d, J = 5.0 Hz), 8.37 (2H, d, J = 5.0 Hz), 9.25 (2H, brs). Anal. Calcd for C$_{30}$H$_{38}$N$_4$O$_6$: C, 65.44; H, 6.96; N, 10.l7. Found: C, 65.27; H, 6.71; N, 10.10.

(j) Sebacic acid: mp 124−125 °C; IR (KBr) 3268, 2934, 2863, 2521, 1915, 1695, 1614, 1585, 1547, 1470, 1436 cm^{-1}; ^{1}H NMR (90 HMHz, CDCl$_3$) δ 1.10−2.47 (30H, m), 6.95 (2H, m), 7.68 (2H, m), 8.15 (2H, d, J = 5.0 Hz), 8.32 (2H, d, J = 5.0 Hz), 9.10 (2H, brs).

(k) Docosanedioic acid: IR (KBr) 3298, 2925, 2858, 2540, 1926, 1701, 1677, 1597, 1581, 1540, 1522, 1466, 1432 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.03−2.47 (54H, m), 7.00 (2H, m), 7.70 (2H, m), 8.24 (4H, m), 9.03 (2H, brs).

(l) Core oxaloleucine retro-bis peptide dicarboxylic acid [HO-Leu-CO-CO-Leu-OH]: IR (KBr) 3386, 2937, 2510, 1920, 1687, 1617, 1558, 1538, 1515, 1435 cm^{-1}; ^{1}H NMR (90 MHz, CDCl3) δ 1.07 (12H, brs), 1.60−2.52 (20H, m), 4.73 (2H, br), 7.27 (4H, m), 7.89 (2H, m), 8.40 (4H, m), 9.41 (2H, brs.)

(m) Core succinoyl retro-bisleucine dicarboxylic acid (HO-Leu-CO-CH$_2$-CH$_2$-CO-Leu-OH): IR (KBr) 3337, 2965, 2548, 1949, 1730, 1709, 1670, 1554, 1525, 1475 cm^{-1}; ^{1}H NMR (90 MHz, CDCl3) δ 0.89 (12H, brs), 1.1−2.80 (24H, br), 4.65 (2H, br), 7.22 (4H, m), 7.80 (2H, m), 8.42 (4H, m), 9.40 (2H, brs).

X-ray Structure Analyses of 1 and Complexes. (1) C$_{22}$H$_{24}$N$_4$O$_2$: $C2/c$, a = 20.784(1) Å, b = 19.753(1) Å, c = 10.609(1) Å, $β$ = 116.54(1)°, V = 3896.5 Å^3, d_{calc} = 1.283 g/cm^3, R = 4.58, Cu Kα radiation.

(2) Perchlorate: C$_{22}$H$_{24}$N$_4$O$_2$·2(HClO$_4$), $Pnma$, a = 11.441(2) Å, b = 32.615(7) Å, c = 6.669(1) Å, V = 2488.5 Å^3, d_{calc} = 1.541 g/cm^3, R = 6.12, Mo Kα radiation.

(3) Copper(II) perchlorate: C$_{22}$H$_{24}$N$_4$O$_2$·Cu(ClO$_4$)$_2$·2H$_2$O, $Pbca$, a = 13.284(3) Å, b = 14.864(2) Å, c = 27.458(3) Å, V = 5421.6 Å^3, d_{calc} = 1.644 g·cm^3, R = 6.8, Mo Kα radiation.

(4) Glutaric acid: C$_{22}$H$_{24}$N$_4$O$_2$·C$_5$H$_8$O$_4$, $P\bar{1}$, a = 10.830(1) Å, b = 10.923(1) Å, c = 11.223(1) Å, $α$ = 76.17(1)°, $β$ = 81.32(1)°, $γ$ = 85.11(1)°, V = 1272.74 Å^3, d_{calc} = 1.327 g/cm^3, R = 8.8, Cu Kα radiation.

(5) Pimelic acid: C$_{22}$H$_{24}$N$_4$O$_2$·C$_7$H$_{12}$O$_4$, $P\bar{1}$, a = 11.263(1) Å, b = 11.720(1) Å, c = 12.411(1) Å, $α$ = 81.078(11)°, $β$ = 67.399(8)°, $γ$ = 66.549(7)°, V = 1387.41 Å^3, d_{calc} = 1.284 g/cm^3, R = 10.8, Cu Kα radiation.

(6) Sebacic acid: C$_{22}$H$_{24}$N$_4$O$_2$·C$_{10}$H$_{18}$O$_4$, $P2_1/c$, a = 11.505(2) Å, b = 16.614(1) Å, c = 16.916(2) Å, $β$ = 104.90(1)°, V = 3124.67 Å^3, d_{calc} = 1.230 g/cm^3, R = 8.8, Cu Kα radiation.

(7) α-Ketoglutaric acid: C$_{22}$H$_{24}$N$_4$O$_2$·C$_5$H$_6$O$_5$, $P\bar{1}$, a = 10.525(5) Å, b = 10.730(5) Å, c = 13.732(4), $α$ = 88.17(2)°, $β$ = 67.84(3) °, $γ$ = 65.33(2) Å, V = 1290.56 Å^3, d_{calc} = 1.345 g/cm^3, R = 4.96, Cu Kα radiation.

(8) Succinic acid: [C$_{22}$H$_{24}$N$_4$O$_2$·C$_4$H$_6$O$_4$]$_2$, $P2_1/n$, a = 12.149(1) Å, b = 15.768(1) Å, c = 13.682(1) Å, $β$ = 107.716(4)°, V = 2496.58 Å^3, d_{calc} = 1.316 g/cm^3, R = 17.1*, Cu Kα radiation. (*Crystals are possibly twinned. A large number of crystals were examined. Twinning mode has not been determined.)

(9) Maleic acid: C$_{22}$H$_{24}$N$_4$O$_2$·2[C$_4$H$_4$O$_4$], $P\bar{1}$, a = 10.942(1) Å, b = 11.112(1) Å, c = 12.960(1) Å, $α$ = 70.04(1)°, $β$ = 88.56(1)°, $γ$ = 74.53(1)°, V = 1423.67 Å^3, d_{calc} = 1.420 g/cm^3, R = 4.7, Cu Kα radiation.

X-ray data were collected on a Siemens automated diffractometer in the $θ/2θ$ mode, constant scan speed of 10 deg/s, 2° scan width, and $2θ_{max}$ = 116° (resolution 0.9 Å for the seven crystals for which Cu Kα was used). For **2** and **3**, data were collected with Mo Kα radiation. Full matrix, anisotropic least-squares refinement was performed on the parameters for all the atoms except the H atoms. H atoms involved in hydrogen bonding were located in electron density maps and, for crystals 5 to 9, their coordinates were refined with isotropic thermal factors. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atom to which each was bonded.

Supporting Information Available: ^{1}H NMR spectra of **1** and complexes with oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, sebacic, docosanedioic acid, α-ketoglutaric, and maleic acid, with retro-bispeptide dicarboxylic acids HO-Leu-CO-CO-Leu-OH and HO-Leu-CO-CH$_2$-CH$_2$-CO-Leu-OH; ^{1}H NMR of perchlorate salt; ^{1}H NMR of complexes of **1** with crotonic acid, phenyl acetic acid, and PGE$_1$; ROESY NMR spectra of glutaric and pimelic acid complexes; FT-IR spectra of dicarboxylic acid complexes of **1** with succinic, glutaric, and pimelic acid in CHCl$_3$ solution; EPR spectra (solid) of copper complex; Figure 1s showing conformation of **1** in perchlorate salt; Figure 2s showing mirror plane symmetry in perchlorate salt; Figure 3s showing cis-cis conformation of **1** in Cu(II) complex; Figure 4s showing pentacoordination to Cu(II); Figure 5s showing a different view of the copper chain; Figure 6s showing stabilization of Cu(II) chain by perchlorate ions; Figure 7s showing connectivity of Cu(II) chains in the third dimension by water molecules; Figure 8s showing the structure of **1**; Figure 9s showing packing of **1**; Figure 10s showing ^{1}H NMR spectra of (a) **1** alone and with (b) glutaric, (c) adipic, (d) pimelic, (e) suberic, and (f) sebacic acid; Figure 11s showing FT-IR spectra of (a) **1**, (b) **1** + perchloric acid, (c) succinic acid, (d) **1** + succinic acid, (e) glutaric acid, (f) **1** + glutaric acid, (g) pimelic acid, and (h) **1** + pimelic acid; Figure 12s showing the square pyramidal polyhedron of Cu(II) complex; crystal structures of the nine crystals including fractional coordinates, bond lengths, bond angles, anisotropic thermal factors, and coordinates for hydrogen atoms (88 pages). See any current masthead page for ordering and Internet access instructions.