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Macrocyclic Diorganotin Complexes of γ -Amino Acid Dithiocarbamates as Hosts for Ion-Pair Recognition

Jorge Cruz-Huerta,[†] Manuel Carillo-Morales,[†] Ericka Santacruz-Juárez,[†] Irán F. Hernández-Ahuactzi,[†] Jaime Escalante-García,[†] Carolina Godoy-Alcantar,[†] Jorge A. Guerrero-Alvarez,[†] Herbert Höpfl,^{*,†} Hugo Morales-Rojas,[†] and Mario Sánchez[‡]

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos,
Av. Universidad 1001, C.P. 62209 Cuernavaca, México, and Facultad de Química, Universidad
de Guanajuato, Noria Alta s/n, C.P. 36050 Guanajuato, México

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The dimethyl-, di-*n*-butyl-, and diphenyltin(IV) dithiocarbamate (dtc) complexes $[\{R_2Sn(L-dtc)\}_x]$ **1–7** (**1**, L = **L1**, R = Me; **2**, L = **L1**, R = *n*-Bu; **3**, L = **L2**, R = Me, x = ∞ ; **4**, L = **L2**, R = *n*-Bu; **5**, L = **L3**, R = Me, x = 2; **6**, L = **L3**, R = *n*-Bu, x = 2; **7**, L = **L3**, R = Ph, x = 2) have been prepared from a series of secondary amino acid (AA) homologues as starting materials: *N*-benzylglycine (α -AA derivative = **L1**), *N*-benzyl-3-aminopropionic acid (β -AA derivative = **L2**), and *N*-benzyl-4-aminobutyric acid (γ -AA derivative = **L3**). The resulting compounds have been characterized by elemental analysis, mass spectrometry, IR and NMR (1H , ^{13}C , and ^{119}Sn) spectroscopy, thermogravimetric analysis, and X-ray crystallography, showing that in all complexes both functional groups of the heteroleptic ligands are coordinated to the tin atoms. By X-ray diffraction analysis, it could be shown that $[\{Me_2Sn(L2-dtc)\}_x]$ (**3**) is polymeric in the solid state, while the complexes derived from **L3** (**5–7**) have dinuclear 18-membered macrocyclic structures of the composition $[\{R_2Sn(L3-dtc)\}_2]$. For the remaining compounds, it could not be established with certainty whether the structures are macrocyclic or polymeric. A theoretical investigation at the B3LYP/SBKJC(d,p) level of theory indicated that the α -AA-dtc complexes might have trinuclear macrocyclic structures. The macrocyclic complexes **5–7** have a double-calix-shaped conformation with two cavities large enough for the inclusion of aliphatic and aromatic guest molecules. They are self-complementary for the formation of supramolecular synthons that give rise to 1D molecular arrangements in the solid state. Preliminary recognition experiments with tetrabutylammonium acetate have shown that the $[\{R_2Sn(L3-dtc)\}_2]$ macrocycles **6** and **7** might interact simultaneously with anions (AcO^-), which coordinate to the tin atoms, and organic cations (TBA^+), which accommodate within the hydrophobic cavity (ion-pair recognition).

1. Introduction

Metal-directed self-assembly is now the method of choice to generate complex, metallosupramolecular architectures having either macrocyclic, cagelike or polymeric structures. For this purpose, small and easily accessible building blocks such as carboxylate and amine ligands are required.¹

Initially, mainly systems with homofunctional ligands have been explored, but today, architectures based on mixed-functional ligands are receiving more and more attention,

since they have advantages for some particular objectives such as the generation of mixed-metal systems with novel optical, electric, and magnetic properties.²

Amino acids and their derivatives are attractive ligands due to their importance in biological systems and have been widely studied;³ however, they frequently act as chelating ligands, thus limiting, if not inhibiting, their

* Author to whom correspondence should be addressed. Fax: (+52) 777 329 79 97. E-mail: hhopfl@ciq.uaem.mx.

[†] Universidad Autónoma del Estado de Morelos.

[‡] Universidad de Guanajuato.

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capacity to link two metal centers. Furthermore, they often have low solubility in organic solvents due to their zwitterionic character.

During the past few years, it has been shown that dithiocarbamate ligands are excellent candidates for crystal engineering⁴ as well as for the preparation of macrocycles,^{5,6} cages,⁷ catenanes,⁸ and nanoparticles.⁹ Albeit dithiocarbamates derived from amino acids have been known for more than 20 years,^{10–12} so far, they have not been explored for applications in metal-directed self-assembly.

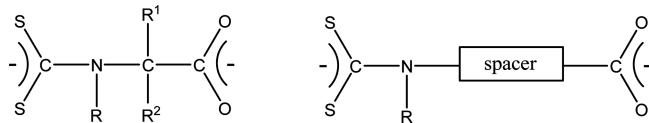
In comparison to systems with transition metals and lanthanides, relatively few macrocyclic and supramolecular assemblies containing main group elements are known. Furthermore, few organometallic species have been involved in self-assembly processes.¹³

Anion and ion pair recognition by Lewis acid moieties has received attention as an important strategy in developing new supramolecular receptors.^{14,15} In this regard, compounds containing organotin(IV) as an electrodeficient center have been previously examined, including macrocycles,¹⁶ cryptand-like¹⁷ and calixarene-shaped receptors¹⁸ as well as acyclic dinuclear receptors,¹⁹ and *N*-confused porphyrins.²⁰ More recently, also ditopic organotin hosts (ion-pair receptors) have been described.²¹

Herein, we report on a series of seven diorganotin complexes that have been prepared from α -, β -, and γ -amino acid dithiocarbamates. The main objective of this study has been to evaluate whether this ligand type allows creation of macrocyclic structures, aside from polymers. Therefore, we

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Chart 1. Schematic Representation of Mixed-Functional Dithiocarbamate Ligands Derived from α -Amino Acids (α -AA) and Homologues with More than One Carbon Atom between the Metal-Coordinating Functions (β - and γ -AA)



employed amino acid dithiocarbamates with a variable number ($n = 1–3$) of methylene group spacers between the metal-coordinating functions (Chart 1). To the best of our knowledge, previously only Sedaghat and Goodarzi have combined organotin moieties with α -amino acid dithiocarbamates.¹² Diorganotin dicarboxylates have been studied extensively,^{13f,22–24} however, the chemistry of diorganotin bis-dithiocarbamates is also almost unexplored so far.⁵

2. Experimental Section

Instrumental. Microwave-assisted reactions were performed in a monomode microwave CEM Discover apparatus with a power output ranging from 0 to 300 W using sealed vessels equipped with condensers. NMR studies were carried out with Varian Gemini 200 and Varian Inova 400 instruments. Standard references were used: TMS ($\delta^{1}\text{H} = 0$, $\delta^{13}\text{C} = 0$) and SnMe₄ ($\delta^{119}\text{Sn} = 0$). To elucidate the structures of the compounds, two-dimensional homo- and heteronuclear correlation spectra (COSY and HSQC) have been carried out for two representative compounds (**6** and **7**) in order to assign the ^{1}H and ^{13}C NMR spectra correctly. IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer. Mass spectra were obtained on a Jeol JMS 700 equipment. Elemental analyses have been carried on Perkin Elmer Series II 2400 and Elementar Vario ELIII instruments, using samples that have been dried previously at 65 °C for 2 h in an Abderhalden equipment. Electronic absorption spectra were recorded at 25 °C on a Hewlett-Packard 8452A diode-array spectrophotometer. Thermogravimetric analyses were performed under nitrogen (50 mL/Min) with a heating rate of 10 °C min⁻¹ using a TA SDT Q600 apparatus.

Preparative Part. Me₂SnCl₂, *n*-Bu₂SnCl₂, Ph₂SnCl₂, N-benzylglycine·HCl, methyl acrylate, and 4-aminobutyric acid (gaba) were commercially available and have been used without further purification.

Preparation of Ligands L2 and L3. For the present study, the *N*-benzyl derivatives of glycine (**L1**), 3-aminopropionic acid (**L2**), and 4-aminobutyric acid (**L3**) were employed, of which only the first was commercially available as hydrogen chloride adduct. The

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methyl ester of *N*-benzyl-3-aminopropionic acid **L2** was prepared according to a reported methodology,²⁵ and then hydrolyzed with NaOH by microwave heating (Scheme S1, Supporting Information). *N*-benzyl-3-aminopropionic acid **L3** has been obtained from the corresponding β^4 -amino acid, 4-aminobutyric acid, according to the reaction sequence shown in Scheme S2 (Supporting Information). In the first step, methyl 4-aminobutyrate was prepared in quantitative yield, which was then benzylated without further purification. Since the 1:1 reaction provided only the 1:2 dibenzylated intermediate, a further reaction step was required, consisting of the microwave-assisted monohydrogenolysis of 4-(dibenzylamino) butyric acid, which afforded *N*-benzyl-4-aminobutyric acid **L3**. For details of the preparation and spectroscopic data, see the Supporting Information.

Preparation of the Diorganotin Complexes 1–7. [Me₂Sn(L1-dtc)]_x, **1.** For the preparation of compound **1**, *N*-benzylglycine·HCl (0.100 g, 0.49 mmol) and three equivalents of KOH (0.083 g, 1.47 mmol) were dissolved in ethanol (20 mL), whereupon an excess of carbon disulfide (2 mL) dissolved in ethanol (10 mL) was added in small portions. After stirring for 2 h at 0 °C, a solution with one equivalent of dimethyltin dichloride (0.108 g, 0.49 mmol) in ethanol (10 mL) was added, giving a white precipitate that was washed with a mixture of ethanol and water (5:1). Yield: 0.149 g (78 %). Mp: 201–203 °C (dec. > 140 °C).

IR (KBr): $\tilde{\nu}$ 3063 (w), 3029 (w), 2922 (w), 2854 (w), 1656 $\nu_{\text{as}}(\text{OCO})$ (s), 1496 $\nu(\text{N}-\text{CSS})$ (s), 1454 (m), 1437 (s), 1410 (m), 1356 $\nu_s(\text{OCO})$ (s), 1272 (m), 1221 (s), 1160 (m), 1080 (w), 994 $\nu_{\text{as}}(\text{SCS})$ (m), 951 (m), 894 (w), 790 (m), 751 (m), 725 (m), 699 (m), 617 (m), 556 (m) cm⁻¹. ¹H NMR (200 MHz, CDCl₃, 20 °C, TMS): δ 1.26 (s, 6H, Sn—CH₃, $J_{\text{Sn}-\text{H}} = 76$ Hz), 4.20 (s, 2H, N—CH₂—COO), 5.03 (s, 2H, N—CH₂—Ph), 7.26–7.35 (m, 5H, C₆H₅). ¹³C NMR (50 MHz, CDCl₃, 20 °C, TMS): δ 8.6 (Sn—CH₃), 55.7 (N—CH₂—COO), 60.0 (N—CH₂—Ph), 128.2, 129.2 (*o*-C₆H₅, *m*-C₆H₅), 128.8 (*p*-C₆H₅), 133.9 (*i*-C₆H₅), 171.2 (COO), 200.5

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51.2 (N—CH₂—CH₂), 58.9 (N—CH₂—Ph), 128.2, 129.4 (*o*-C₆H₅, *m*-C₆H₅), 128.8 (*p*-C₆H₅), 134.7 (*i*-C₆H₅), 176.5 (COO), 199.3 (CSS). ¹¹⁹Sn NMR (74.5 MHz, CDCl₃, SnMe₄, 20 °C): δ = 221.1 (Δν_{1/2} = 28 Hz). MS (FAB⁺): *m/z* (%) 404 ([M + H]⁺, 7). High resolution MS (FAB⁺) for C₁₃H₁₈O₂NS₂Sn ([M + H]⁺): *m/z* (%) 403.9833 (10); error, +7.9 ppm. Anal. calcd for C₁₃H₁₇NO₂S₂Sn (402.12): C, 38.83; H, 4.26; N, 3.48. Found: C, 38.47; H, 4.48; N, 3.50.

[ⁿBu₂Sn(L2-dtc)]_x, **4**. Compound **4** was obtained in the form of a white precipitate using the procedure described for compound **3**. Yield: 82 %. Mp: 249–250 °C (dec. > 90 °C). IR (KBr): ν 3037 (w), 2956 (m), 2921 (m), 2859 (w), 1621 ν_{as}(OCO) (s), 1487 ν(N—CSS) (m), 1435 (m), 1381 ν_s(OCO) (s), 1286 (m), 1248 (m), 1198 (w), 1148 (w), 1071 (w), 1045 (w), 981 and 955 ν_{as}(SCS) (m), 955 (m), 878 (w), 793 (w), 744 (m), 694 (m), 635 (m), 587 (m), 547 (m) cm^{−1}. ¹H NMR (400 MHz, CDCl₃, 20 °C, TMS): δ 0.93 (t, 6H, δ-CH₃), 1.43 (m, 4H, γ-CH₂), 1.80 (m, 8H, α-CH₂, β-CH₂), 2.70 (t, 2H, CH₂—CH₂—COO[−]), 3.92 (t, 2H, N—CH₂—CH₂), 5.08 (s, 2H, N—CH₂—Ph), 7.33 (m, 5H, C₆H₅). ¹³C NMR (100 MHz, CDCl₃, 20 °C, TMS): δ 14.1 (δ-CH₃), 26.6 (γ-CH₂), 27.7, 28.2 (α-CH₂, β-CH₂), 33.2 (CH₂—CH₂—COO), 51.2 (N—CH₂—CH₂), 58.8 (N—CH₂—Ph), 127.8, 129.1 (*o*-C₆H₅, *m*-C₆H₅), 128.4 (*p*-C₆H₅), 134.7 (*i*-C₆H₅), 176.3 (COO), 199.8 (CSS). ¹¹⁹Sn NMR (74.5 MHz, CDCl₃, SnMe₄, 20 °C): δ = 230.8 (Δν_{1/2} = 13 Hz). MS (FAB⁺): *m/z* (%) 488 ([M + H]⁺, 18). High resolution MS (FAB⁺) for C₁₉H₃₀O₂NS₂Sn ([M + H]⁺): *m/z* (%) 488.0728 (71); error, −2.5 ppm. Anal. calcd for C₁₉H₂₉NO₂S₂Sn (486.28): C, 46.93; H, 6.01; N, 2.88. Found: C, 46.92; H, 6.05; N, 3.09.

[Me₂Sn(L3-dtc)]₃, **5**. Compound **5** was obtained in the form of a white precipitate using the procedure described for compound **3**.

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Crystals suitable for X-ray analysis could be obtained upon recrystallization from a mixture of dichloromethane and hexane (2:1). Yield: 66 %. Mp: 155–157 °C (dec. > 120 °C). IR (KBr): ν 3031 (w), 2926 (w), 1623 ν_{as}(OCO) (s), 1496 ν(N—CSS) (s), 1452 (m), 1425 (m), 1360 ν_s(OCO) (s), 1322 (m), 1299 (m), 1252 (m), 1224 (m), 1137 (m), 1082 (w), 1051 (w), 1029 (w), 981 ν_{as}(SCS) (w), 900 (w), 861 (w), 777 (m), 750 (m), 701 (w), 672 (w), 560 (w), 519 (w), 496 (w), 455 (w), 408 (w) cm^{−1}. ¹H NMR (200 MHz, CDCl₃, 20 °C, TMS): δ 1.19 (s, 12H, Sn—CH₃, ²J_{Sn-H} = 78 Hz), 1.95 (m, 4H, CH₂—CH₂—CH₂), 2.30 (t, 4H, CH₂—CH₂—COO), 3.77 (t, 4H, N—CH₂—CH₂), 5.02 (s, 4H, N—CH₂—Ph), 7.27–7.37 (m, 10H, C₆H₅) ppm. ¹³C NMR (100 MHz, CDCl₃, 20 °C, TMS): δ = 8.4 (Sn—CH₃), 22.2 (CH₂—CH₂—CH₂), 32.1 (CH₂—CH₂—COO), 54.4 (N—CH₂—CH₂), 57.6 (N—CH₂—Ph), 127.7, 129.1 (*o*-C₆H₅, *m*-C₆H₅), 128.4 (*p*-C₆H₅), 134.5 (*i*-C₆H₅), 178.0 (COO), 199.6 (CSS). ¹¹⁹Sn NMR (149.1 MHz, CDCl₃, SnMe₄, 20 °C): δ = 223.7 (Δν_{1/2} = 17 Hz). MS (FAB⁺): *m/z* (%) 418 ([M_{monomer} + H]⁺, 100), 817 ([M_{dimer} — CH₃]⁺, 58), 833 ([M_{dimer} + H]⁺, 20), 1248 ([M_{trimer} + H]⁺, 2), 1665 ([M_{tetramer} + H]⁺, 2). Anal. calcd for C₂₈H₃₈N₂O₄S₄Sn₂ (832.29): C, 40.41; H, 4.60; N, 3.37. Found: C, 40.20; H, 4.52; N, 3.38.

[ⁿBu₂Sn(L3-dtc)]₃, **6**. Compound **6** was obtained in the form of a white precipitate using the procedure described for compound **3**. Crystals suitable for X-ray analysis could be obtained upon recrystallization from a mixture of dichloromethane and hexane (2:1). Yield: 53 %. Mp: 139–140 °C. IR (KBr): ν 3029 (w), 2956 (m), 2923 (s), 2869 (m), 2854 (m), 1622 ν_{as}(OCO) (s), 1495 ν(N—CSS) (s), 1450 (s), 1425 (m), 1357 ν_s(OCO) (m), 1323 (m), 1306 (m), 1297 (m), 1255 (w), 1222 (m), 1144 (m), 1081 (w), 1027 (w), 984 and 967 ν_{as}(SCS) (m), 921 (w), 900 (w), 863 (w), 844 (w), 779 (m), 740 (m), 696 (m), 671 (m), 644 (w), 629 (w), 591 (w), 545 (w), 495 (w), 452 (w) cm^{−1}. ¹H NMR (200 MHz, CDCl₃, 20 °C, TMS): δ 0.91 (t, 12H, δ-CH₃), 1.42 (m, 8H, γ-CH₂), 1.79 (m, 16H, α-CH₂, β-CH₂), 1.95 (m, 4H, CH₂—CH₂—CH₂), 2.28 (t, 4H, CH₂—CH₂—COO), 3.78 (t, 4H, N—CH₂—CH₂), 5.05 (s, 4H, N—CH₂—Ph), 7.26–7.33 (m, 10H, C₆H₅) ppm. ¹³C NMR (50 MHz, CDCl₃, 20 °C, TMS): δ 14.1 (δ-CH₃), 22.4 (CH₂—CH₂—CH₂), 26.6 (γ-CH₂), 27.8, 28.2 (α-CH₂, β-CH₂), 32.1 (CH₂—CH₂—COO), 54.5 (N—CH₂—CH₂), 57.4 (N—CH₂—Ph), 127.6, 129.1 (*o*-C₆H₅, *m*-C₆H₅), 128.3 (*p*-C₆H₅), 134.9 (*i*-C₆H₅), 178.1 (COO), 200.7 (CSS). ¹¹⁹Sn NMR (149.1 MHz, CDCl₃, SnMe₄, 20 °C): δ = 230.2 (Δν_{1/2} = 44 Hz). MS (FAB⁺): *m/z* (%) 502 ([M_{monomer} + H]⁺, 100), 943 ([M_{dimer} — n-Bu]⁺, 33), 1001 ([M_{dimer} + H]⁺, 10), 1501 ([M_{trimer} + H]⁺, 1), 2001 ([M_{tetramer} + H]⁺, 1). Anal. calcd for C₄₀H₆₂N₂O₄S₄Sn₂ (1000.61): C, 48.01; H, 6.25; N, 2.80. Found: C, 47.67; H, 6.06; N, 2.88.

[Ph₂Sn(L3-dtc)]₃, **7**. Compound **7** was obtained in the form of a white precipitate using the procedure described for compound **3**. Crystals suitable for X-ray analysis could be obtained upon recrystallization from a mixture of dichloromethane and hexane (2:1). Yield: 54 %. Mp: 183–184 °C. IR (KBr): ν 3059 (w), 2925 (w), 1643 and 1616 ν_{as}(OCO) (m), 1496 ν(N—CSS) (s), 1450 (m), 1478 (m), 1361 ν_s(OCO) (m), 1299 (m), 1260 (m), 1226 (s), 1143 (m), 1073 (w), 1024 (w), 990 and 971 ν_{as}(SCS) (w), 971 (w), 914

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(w), 860 (w), 780 (m), 732 (s), 695 (s), 624 (w), 498 (w), 450 (m) cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , 20 $^\circ\text{C}$, TMS): δ 1.98 (m, 4H, $\text{CH}_2-\text{CH}_2-\text{CH}_2$), 2.31 (t, 4H, $\text{CH}_2-\text{CH}_2-\text{COO}$), 3.81 (t, 4H, $\text{N}-\text{CH}_2-\text{CH}_2$), 4.96 (s, 4H, $\text{N}-\text{CH}_2-\text{Ph}$), 7.21–7.39 (m, 11H, $\text{CH}_2-\text{C}_6\text{H}_5$, *m*- SnC_6H_5 , *p*- SnC_6H_5), 7.88 (m, 4H, $^3J_{\text{Sn}-\text{H}} = 84$ Hz, *o*- SnC_6H_5). ^{13}C NMR (100 MHz, CDCl_3 , 20 $^\circ\text{C}$, TMS): δ 22.8 ($\text{CH}_2-\text{CH}_2-\text{CH}_2$), 31.9 ($\text{CH}_2-\text{CH}_2-\text{COO}$), 54.7 ($\text{N}-\text{CH}_2-\text{CH}_2$), 57.6 ($\text{N}-\text{CH}_2-\text{Ph}$), 127.8, 128.5, 128.9, 129.1, 129.9 (*o*-, *m*-, *p*- $\text{CH}_2\text{C}_6\text{H}_5$, *m*-, *p*- SnC_6H_5), 134.2 (*i*- $\text{CH}_2\text{C}_6\text{H}_5$), 135.7 (*o*- SnC_6H_5), 178.5 (COO), 198.2 (CSS). ^{119}Sn NMR (149.1 MHz, CDCl_3 , SnMe_4 , 20 $^\circ\text{C}$): δ -371.6 ($\Delta\nu_{1/2} = 22$ Hz). MS (FAB $^+$): m/z (%) 542 ([$M_{\text{monomer}} + \text{H}]^+$, 100), 1003 ([$M_{\text{dimer}} - \text{Ph}]^+$, 27), 1081 ([$M_{\text{dimer}} + \text{H}]^+$, 5), 1622 ([$M_{\text{trimer}} + \text{H}]^+$, 2). Anal. calcd for $\text{C}_{48}\text{H}_{46}\text{N}_2\text{O}_4\text{S}_4\text{Sn}_2$ (1080.57): C, 53.35; H, 4.29; N, 2.59. Found: C, 52.77; H, 4.25; N, 2.86.

X-Ray Crystallography. X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ($\lambda_{\text{MoK}\alpha} = 0.71073$ Å; monochromator, graphite). Frames were collected at $T = 293$ K (compound **7**), $T = 173$ K (compounds **3** and **6**), and $T = 100$ K (**L2** and compound **5**) via ω/ϕ rotation at 10 s per frame (SMART).^{26a} The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT).^{26b} Corrections were made for Lorentz and polarization effects. Structure solution, refinement, and data output were carried out with the SHELXTL-NT program package.^{26c,d} Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. For **L2**, the hydrogen atoms of the R_2NH_2^+ function have been localized by difference Fourier maps. For compound **3**, only crystals of low quality ($R_{\text{int}} = 0.107$) could be grown. Because of the weak diffraction, reflections have been included only up to $\theta = 23.0$ for the refinement; however, the data were of sufficient quality to determine the molecular and the crystal structure. Solvent molecules (benzene) are present in the crystal lattice of this compound. In the final electron density map of compound **3**, there are three peaks with residual electron densities ranging from $\Delta\rho = 1.46$ to 1.11 $e\text{\AA}^{-3}$, which, however, are located in the proximity of the tin atoms. There was no further peak with a residual electron density larger than $\Delta\rho = 0.89 e\text{\AA}^{-3}$. In the crystal structure of compound **6**, one of the Sn-*n*-butyl groups is disordered over two positions (occ. factors 0.41 and 0.59), and DFIX and EADP instructions have been used for the refinement of this function. In the final electron density map of this compound, there is a peak near one of the tin atoms with a residual electron density of $\Delta\rho = 1.27 e\text{\AA}^{-3}$; however, there was no further peak with a residual electron density larger than $\Delta\rho = 0.64 e\text{\AA}^{-3}$. The asymmetric unit of compound **7** contains two independent molecule halves. Molecular structures were illustrated by the SHELXTL-NT software package^{26d} and MERCURY.²⁷ Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-686293–CCDC-686297. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ,

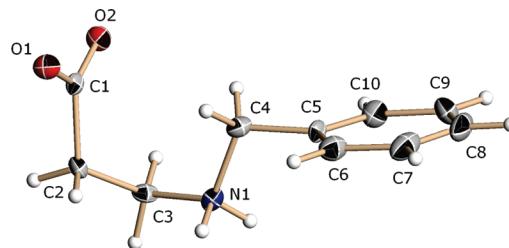


Figure 1. Perspective view of the molecular structure of **L2**.

U.K. (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk).

Computational Details. The quantum chemical calculations were performed using the GAMESS program package.²⁸ The B3LYP^{29,30} exchange correlation potential was used for optimizing energies in conjugation with the SBKJC(d,p) basis set.^{31–33} Harmonic vibrational frequencies were computed at the same level of theory to characterize stationary points as minima. All structures were visualized with the Chemcraft program.³⁴

Recognition Experiments. The anion binding capacities between macrocycles **6** and **7** and tetrabutylammonium acetate (AcOTBA) were evaluated both by UV-vis and NMR titration experiments. In the UV-vis titration experiments, successive aliquots of a solution of AcOTBA in CHCl_3 were added to a solution of **6** or **7** in CHCl_3 (2.5 mL, 3.3×10^{-5} M), and the spectral changes were monitored within a range of $\lambda = 230$ –400 nm. In the ^1H NMR titration experiments, aliquots of AcOTBA were added up to 2.3 molar equivalents at 25 $^\circ\text{C}$ to a solution of macrocycle **6** (3.3×10^{-2} M) or **7** (3.0×10^{-2} M) in CDCl_3 .

3. Results and Discussion

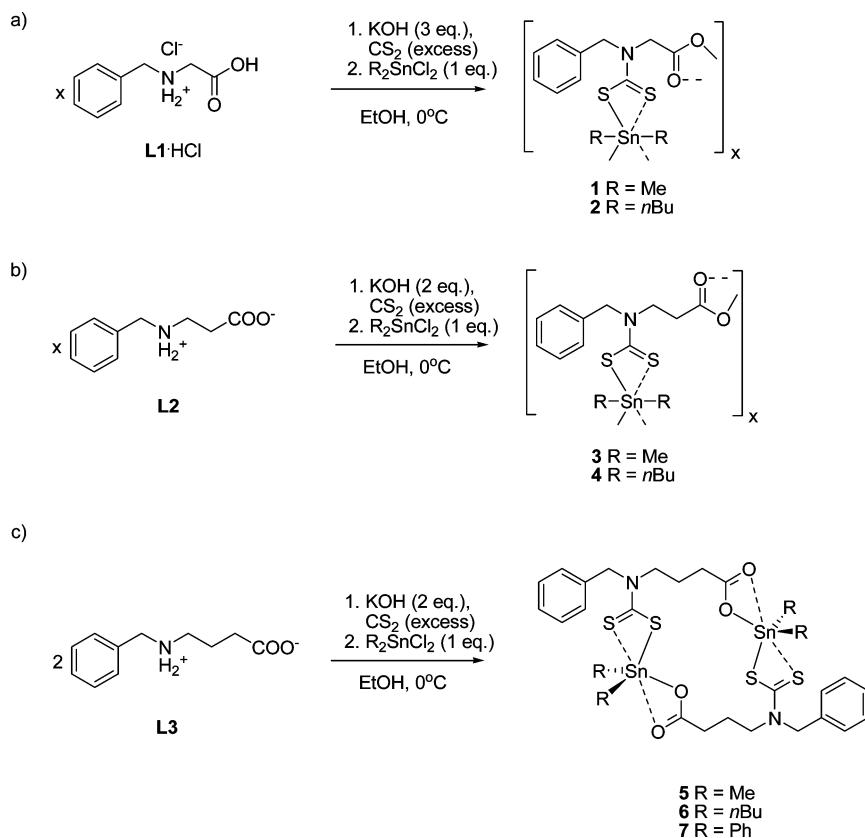
3.1. Preparation and Spectroscopic Characterization.

The coordination chemistry of mono-dithiocarbamates is well-known, and generally secondary amines are used as starting materials for the ligand preparation, as these give more stable complexes.³⁵ For the present study, the *N*-benzyl derivatives of glycine (**L1**), 3-aminopropionic acid (**L2**), and 4-aminobutyric acid (**L3**) were employed. The benzylated β -amino acid **L2** was obtained in crystalline form so that its solid-state structure could be determined by X-ray diffraction analysis. The molecular structure shown in Figure 1 evidences its zwitterionic character ($\text{C}-\text{O}^- = 1.237(6)$ and $1.247(5)$ Å), which is in agreement with the IR and NMR spectroscopic data (vide infra).

For the preparation of the diorganotin complexes **1**–**7**, the secondary amino acids were transformed to their potassium dithiocarbamate salts, which were then combined in ethanol with the corresponding diorganotin(IV) dichloride (Scheme

- (26) (a) SMART: Bruker Molecular Analysis Research Tool, versions 5.057, 5.618; Bruker Analytical X-ray Systems: Madison, WI, 1997, 2000. (b) SAINT + NT, versions 6.01, 6.04; Bruker Analytical X-ray Systems: Madison, WI, 1999, 2001. (c) Sheldrick, G. M. SHELX86, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1986. (d) SHELXTL-NT, versions 5.10, 6.10; Bruker Analytical X-ray Systems: Madison, WI, 1999, 2000.
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Scheme 1. Reaction Sequences for the Preparation of Compounds **1–7**

1). The yields varied from 38 to 89%. All compounds are white solids, with the exception of compound **2**, which is a light-yellow viscous oil. Unfortunately, the diphenyltin derivatives of **L1-dtc** and **L2-dtc** could not be obtained in pure form.

All compounds have been characterized as far as possible by elemental analysis, FAB mass spectrometry (positive ion mode), IR and NMR (^1H , ^{13}C , and ^{119}Sn) spectroscopy, thermogravimetric analysis, and single-crystal X-ray diffraction (compounds **3**, **5**, **6**, and **7**).

Since metal-coordinated dithiocarbamate and carboxylate functions generate relatively strong, characteristic vibrations, valuable structural information could be extracted from the IR spectra of compounds **1–7**. The chelation of the carboxylate groups to the diorganotin moieties is anisobidentate. This is indicated by the symmetric and asymmetric $\nu(\text{OCO})$ vibrations at 1656 – 1616 cm^{-1} for $\nu_{\text{as}}(\text{OCO})$ and 1380 – 1342 cm^{-1} for $\nu_{\text{s}}(\text{OCO})$. For comparison, the values for the $\nu(\text{C=O})$ vibration of metal-free carboxyl groups vary from 1725 to 1680 cm^{-1} , while for alkali metal carboxylates, the asymmetric $\nu_{\text{as}}(\text{OCO})$ and symmetric $\nu_{\text{s}}(\text{OCO})$ vibrations are in the range of 1578 – 1571 cm^{-1} and 1414 – 1402 cm^{-1} , respectively.³⁶ N-alkyl stretching generates bands in the region of 1250 – 800 cm^{-1} . The N–CSS bonds in the dithiocarbamate functions of compounds **1–7** vibrate at higher wavenumbers, 1503 – 1486 cm^{-1} , because of the partial delocalization of π -electron density. Two bands are generally observed for the CS_2 groups, one in the range of

1050 – 950 cm^{-1} for the asymmetric $\nu_{\text{as}}(\text{SCS})$ vibration and the other one at approximately 700 – 450 cm^{-1} for the symmetric $\nu_{\text{s}}(\text{SCS})$ vibration. For compounds **1–7**, only the $\nu_{\text{as}}(\text{SCS})$ vibrations could be identified unequivocally (1014 – 955 cm^{-1}). Because the $\nu(\text{N-alkyl})$ and $\nu_{\text{as}}(\text{SCS})$ vibrations have similar frequencies, frequent coupling is observed.^{10,37}

A theoretical, exemplary investigation at the B3LYP/SBKJC(d,p) level of theory has been carried out for compound **5** to confirm that the above-described assignations were correct. The geometry of the calculated molecular structure of compound **5** (Table S1, Supporting Information) is in very good agreement with the experimentally determined solid-state structure (vide infra). The same is true for the calculated and experimental vibrational frequencies (Table S2, Supporting Information). For a comparison of the spectra, see Figure S1 in the Supporting Information.

The ^1H and ^{13}C NMR spectra of compounds **1–7** were assigned completely employing two-dimensional $^1\text{H}\{\text{H}\}$ and $^1\text{H}\{\text{C}\}$ experiments (COSY and HSQC) for two representative examples (compounds **6** and **7**). A comparison of the ^1H NMR spectra between the starting *N*-benzylated amino acids and the resulting products **1–7** (Table S3, Supporting Information) showed significant shift displacements to lower fields for the

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$N-CH_2$ methylene hydrogen atoms ($\Delta\delta = 0.72 - 0.94$ ppm for $N-CH_2-Ph$ and $\Delta\delta = 0.34 - 0.80$ ppm for the $N-CH_2$ -spacer group). Low-field shifts are also observed from the ^{13}C NMR spectra: $\Delta\delta = 5.4 - 8.9$ ppm for $N-CH_2-Ph$ and $\Delta\delta = 5.1 - 8.8$ ppm for the $N-CH_2$ -spacer group. The CO_2 and NCS_2 groups gave ^{13}C NMR signals in the range of $\delta = 170.8 - 178.5$ ppm and $\delta = 198.2 - 200.8$ ppm, respectively, in agreement with previously reported data.³⁸ Interestingly, in the 1H NMR spectra, the signals for the methylene hydrogen atoms are broadened, indicating that the complexes are involved in at least one dynamic process. Both intra- and intermolecular ligand exchange reactions and configurational and conformational equilibria are possible.^{24,39} The integration of the 1H NMR spectra indicates that the composition of compounds **1–7** is $\{[R_2Sn(L-dtc)]_x\}$ ($L = N$ -benzyl amino acid), with either cyclic or polymeric structures.

The ^{119}Sn NMR chemical shifts for the dialkyltin complexes **1–6** vary from $\delta = -216.5$ to -230.8 ppm (Table S3, Supporting Information), this being a typical range for penta- to hexa-coordinated diorganotin complexes.⁴⁰ For the diphenyltin derivative **7**, the ^{119}Sn NMR shift displacement is $\delta = -370.3$ ppm. The upfield shift in comparison to the dialkyltin complexes by approximately $\Delta\delta = 150$ ppm is well-documented.⁴¹

The mass spectra (FAB^+) of compounds **1** and **2** gave peaks for species having monomeric, dimeric, and trimeric composition, which could indicate the formation of a trinuclear macrocycle, $\{[R_2Sn(L-dtc)]_3\}$. A theoretical investigation at the B3LYP/SKBCJ(d,p) level of theory for compound **1** has shown that the trimer $\{[Me_2Sn(L-dtc)]_3\}$ has a structure and conformation that is related to previously reported trinuclear diorganotin dicarboxylates (Figure 2; Table S4, Supporting Information).^{23e-h,k,m,n,24a-d} However, it cannot be excluded that these peaks are the result of polymer fragmentation or fragment reaggregation. For compounds **3** and **4**, only peaks for monomer fragments were found, albeit the single X-ray diffraction analysis of compound **4** revealed a polymeric structure in the solid state (vide infra). For compounds **5–7**, peaks for monomeric, dimeric, trimeric, and tetrameric (only for **5** and **6**) species were detected.

3.2. X-Ray Crystallographic Study. Compounds **3**, **5**, **6**, and **7** gave single crystals that were suitable for X-ray diffraction analysis. The molecular structures are shown in Figures 3 and 4. The most relevant crystallographic data and selected geometric parameters are summarized in Tables 1 and 2. For the sake of comparison, in Table 2, the geometric data for the cal-

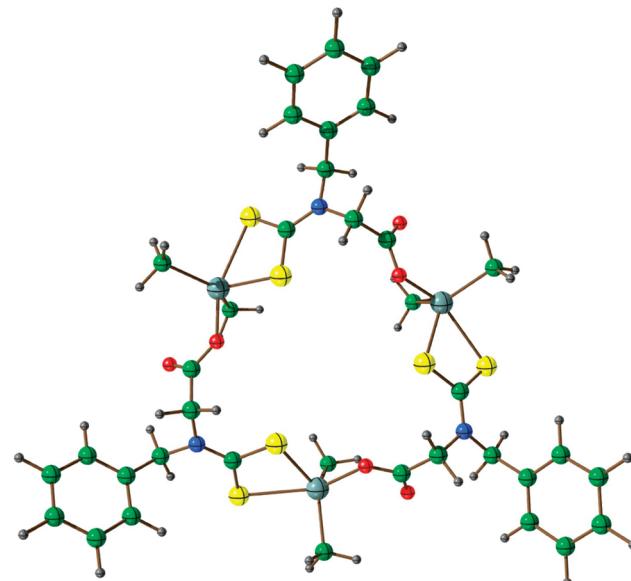


Figure 2. Calculated molecular structure for trimer $\{[Me_2Sn(L1-dtc)]_3\}$ (level of theory: B3LYP/SKBCJ(d,p)).

culated structures of compounds **1** and **5** have been also included.

The solid-state structure of compound **3** consists of linear polymeric chains having only translational symmetry (Figure 3). Within the polymer, the tin–tin distances are 9.82 Å. The tin centers are hexa-coordinate having a skewed-trapezoidal-bipyramidal geometry, in which the axial positions are occupied by the methyl groups. This can be seen from the C–Sn–C bond angle that is intermediate between the values found for complexes with cis- and trans-substituted octahedral geometries.⁴² The Me–Sn–Me bond angle found in the solid-state structure agrees well with the value calculated from the $^2J_{Sn-H}$ coupling constant in solution (found, 132.9(8) ; calcd., 127.2),⁴³ thus indicating that the coordination geometries are similar. The trapezoidal planes are formed by the oxygen and sulfur atoms of the chelating carboxylate and dithiocarbamate groups. Both functions are coordinated in an anisobidentate manner ($Sn-O = 2.171(11)$ Å, $Sn \cdots O = 2.803(11)$ Å, $Sn-S = 2.493(5)$, and $Sn \cdots S = 2.743(5)$ Å), as is commonly observed for diorganotin carboxylates²⁴ and dithiocarbamates.^{5,44,45} Within the dithiocarbamate function, the N–CSS bond length

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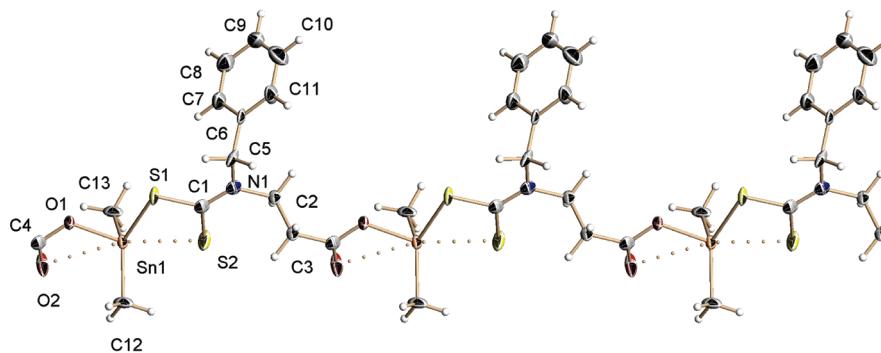


Figure 3. Fragment of the polymeric solid-state structure of compound 3. Ellipsoids are shown at the 50 % probability level.

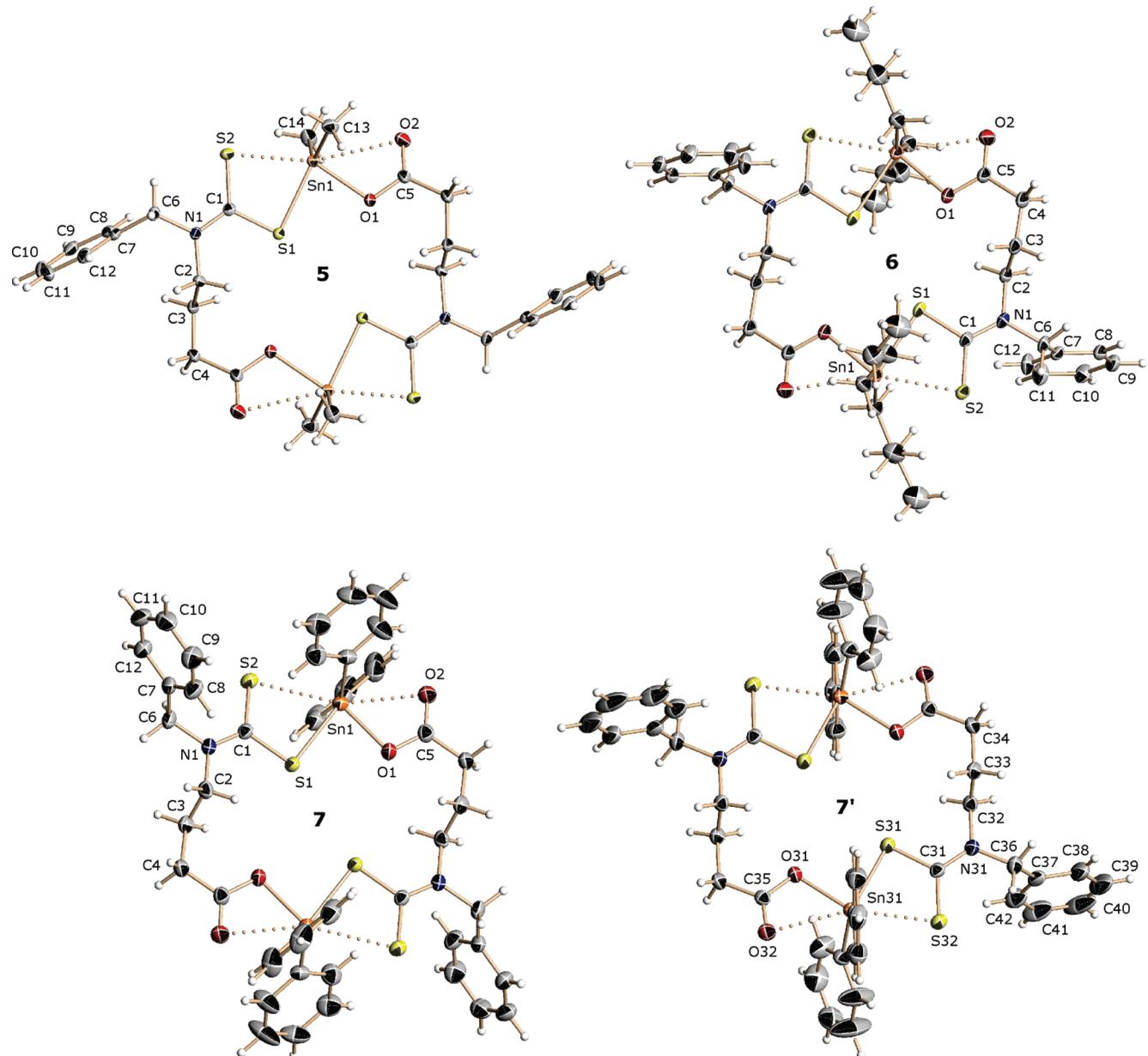


Figure 4. Perspective views of the molecular structures of compounds 5, 6, and 7. Ellipsoids are shown at the 50% (5) and 30% (6, 7, and 7') probability levels.

of 1.32(2) Å indicates substantial delocalization of π -electron density in this bond.

Compounds 5–7 have dinuclear 18-membered $\{C_{10}N_2O_2S_2Sn_2\}$ macrocyclic structures (Figure 4) and display

symmetry, each being disposed about a crystallographic center of inversion (point group: C_i). For the diphenyltin complex, there are two independent molecules in the unit cell (7 and 7').

Table 1. Crystallographic Data for Compounds **L2**, **3**, **5**, **6**, and **7**

crystal data ^a	L2	3	5	6	7
formula	C ₁₀ H ₁₃ NO ₂	C ₁₃ H ₁₇ NO ₂ S ₂ Sn, C ₆ H ₆	C ₂₈ H ₃₈ N ₂ O ₄ S ₄ Sn ₂	C ₄₀ H ₆₂ N ₂ O ₄ S ₄ Sn ₂	C ₄₈ H ₄₆ N ₂ O ₄ S ₄ Sn ₂
MW (g mol ⁻¹)	179.21	480.19	832.22	1000.54	1080.49
space group	Pca2 ₁	P2 ₁ /c	P2 ₁ /c	P ₁	P ₁
temp. (K)	100(2)	173(2)	100(2)	173(2)	293(2)
<i>a</i> (Å)	10.3641(11)	9.8234(14)	9.0547(6)	10.2065(8)	8.9106(5)
<i>b</i> (Å)	9.4025(10)	21.045(3)	22.8219(16)	11.0423(9)	14.7125(9)
<i>c</i> (Å)	9.2553(10)	10.7594(16)	7.7988(5)	11.2547(9)	19.5145(12)
α (deg)	90	90	90	67.704(1)	109.930(1)
β (deg)	90	101.182(3)	97.684(1)	75.579(1)	96.726(1)
γ (deg)	90	90	90	82.665(1)	98.289(1)
<i>V</i> (Å ³)	901.91(17)	2182.1(6)	1597.12(18)	1135.85(16)	2341.6(2)
<i>Z</i>	4	4	2	1	2
μ (mm ⁻¹)	0.092	1.373	1.861	1.322	1.290
ρ_{calcd} (g cm ⁻³)	1.320	1.462	1.731	1.463	1.532
$R^{b,c}$	0.065	0.129	0.025	0.041	0.041
$R_w^{d,e}$	0.127	0.226	0.068	0.105	0.091

^a $\lambda_{\text{MoK}\alpha} = 0.71073$ Å. ^b *I* > 2σ(*I*). ^c *R* = $\sum(F_o^2 - F_c^2)/\sum F_o^2$. ^d All data. ^e $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths [Å], Bond Angles [deg], and Intermolecular Interactions [Å] for Calculated (Compounds **1** and **5**) and Experimental Structures (Compounds **3**, **5**, **6**, and **7**)

	1 _{calcd} ^a	3 _{X-ray}	5 _{X-ray}	5 _{calcd} ^a	6 _{X-ray} ^b	7 _{X-ray} ^c
Bond Lengths (Å)						
Sn—C	2.13 2.13	2.105(16) 2.095(19)	2.109(3) 2.117(3)	2.13 2.13	2.103(9) 2.131(5)	2.103(4) 2.113(3) 2.121(4) 2.122(4)
Sn—O	2.14	2.171(11)	2.135(2)	2.12	2.145(3)	2.113(3) 2.120(3)
Sn···O	3.12	2.803(11)	2.924(2)	2.91	2.868(3)	2.684(3) 2.779(3)
Sn—S	2.50	2.493(5)	2.493(1)	2.51	2.480(1)	2.458(1) 2.460(1)
Sn···S	2.82	2.744(5)	2.734(1)	2.88	2.771(1)	2.783(1) 2.861(1)
C—S	1.77 1.74	1.758(19) 1.71(2)	1.743(3) 1.711(3)	1.77 1.73	1.739(4) 1.710(4)	1.749(4) 1.688(4) 1.752(4) 1.695(4)
N—CSS	1.35	1.32(2)	1.327(4)	1.36	1.323(5)	1.321(5) 1.325(5)
Bond Angles (deg)						
C—Sn—C	125.9	132.9(8)	127.97(14)	129.8	127.6(3) 144.8(4)	132.43(17) 132.49(16)
O—Sn—O	46.6	50.3(6)	49.1(11)	50.3	49.9(3)	51.21(15) 52.75(15)
S—Sn—S	68.4	68.41(15)	68.52(2)	67.4	68.29(3)	66.96(3) 68.47(3)
O _{cov} —Sn—S _{cov}	81.4	80.7(3)	81.18(6)	83.5	81.66(9)	81.10(8) 84.24(8)
O _{coord} ···Sn···S _{coord}	163.8	160.3(3)	162.3(6)	158.9	159.95(9)	156.25(8) 159.13(8)
O—C—O	124.9	120.3(17)	123.2(3)	122.6	122.7(4)	120.6(4) 122.0(4)
S—C—S	117.6	116.6(11)	117.31(17)	118.2	118.0(2)	118.4(2) 118.5(2)
Others (Å)						
Sn···Sn _{transannular}	7.70		7.10	7.10	7.07	6.80 7.07
S···S _{transannular}	5.55		3.67	3.81	3.54	3.73 3.63

^a Level of theory: B3LYP/SKBCJ(d,p). ^b One of the Sn-*n*-butyl groups is disordered over two positions. ^c Two independent molecule halves in the asymmetric unit.

The transannular Sn···Sn distances for **5**, **6**, **7**, and **7'** are 7.10, 7.07, 7.07, and 6.80 Å, respectively, and the corresponding S···S distances are 3.67, 3.54, 3.73, and 3.63 Å. It is interesting to note that the Sn···Sn and S···S distances are significantly different for **7** and **7'**, thus indicating that the molecular structures possess certain flexibility. This is evidenced by the perspective views given in Figure 4,

showing different orientations of the phenyl groups as a consequence of C—H···π interactions in the crystal lattice.

As for compound **3**, the tin atoms have skewed-trapezoidal-bipyramidal coordination environments with anisobidentate chelation modes of the coordinating functions. The C—Sn—C bond angles vary from 127.6(3) to 144.8(4), and for the dimethyltin derivative, the Me—Sn—Me bond angle found

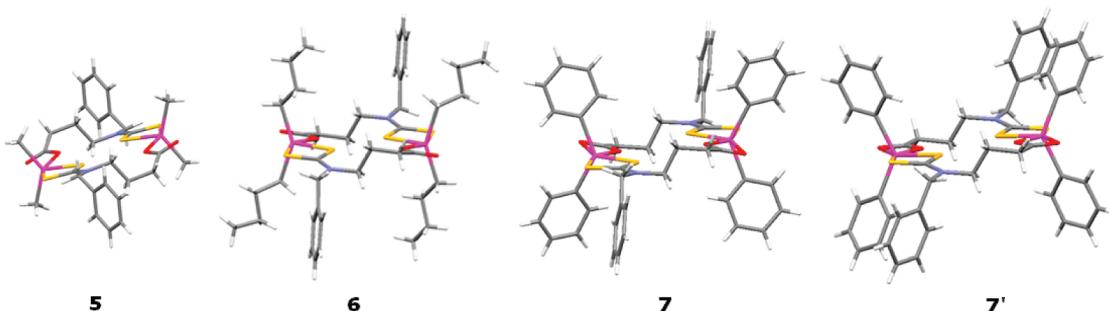


Figure 5. Lateral views of the molecular structures of compounds **5**, **6**, **7**, and **7'**.

in the solid state agrees very well with the value calculated from the $^2J_{\text{Sn}-\text{H}}$ coupling constant in solution (found, 128.0(1); calcd., 128.4).⁴³ The covalent Sn–O and Sn–S bonds are very similar for the three compounds, 2.113(3)–2.145(3) Å and 2.458(1)–2.493(1) Å, respectively. In the case of the coordinative Sn···O and Sn···S distances, the differences are larger, 2.684(3)–2.924(2) and 2.734(1)–2.861(1) Å, respectively. The bonding asymmetry of the ligands is reflected in the C–S bond lengths (1.688(4)–1.711(3) Å versus 1.739(4)–1.752(4) Å). The N–CS₂ bond lengths are in the range from 1.321(5) to 1.327(4) Å. Recently, the geometric parameters for 171 organic dithiocarbamate esters have been revised, giving mean values for C=S, C–S, and N–CSS of 1.658(1), 1.758(2), and 1.346(2) Å, respectively.⁴⁶ A comparison with the values determined herein for compounds **3**, **5**, **6**, and **7** shows clearly that the delocalization within the NCS₂ fragment is increased upon coordination to the diorganotin fragment: the N–CSS and C–S bonds are shortened, while the C=S bonds are elongated (Table 2).

A comparison of the calculated and experimental geometric data for compound **5** shows that the level of theory employed herein for the geometry optimization of diorganotin dithiocarbamates is adequate for a proper computational analysis. This is confirmed by the structural analysis of compound **1**, which shows that also in this case the bond lengths and bond angles are within the range observed for those compounds that have been characterized by X-ray diffraction.

As a result of the varying steric strain of the organic groups attached to the tin atoms, there are slight differences in the approximate chair conformations of the three macrocycles and even between the two independent molecules present in the crystal lattice of **7** (Figure 5). The differences can be also seen from the dihedral angles formed between the mean planes of the carboxylate and dithiocarbamate groups attached to the tin atoms. The values are 14.1, 5.1, 1.8, and 5.8° for compounds **5**, **6**, **7**, and **7'**, respectively.

The macrocyclic cavity of compounds **5**–**7** is not large enough for the inclusion of guest molecules or ions; however, the lateral views shown in Figure 5 reveal a double-calix-shaped conformation, in particular for compounds **6** and **7**, which might be adequate for molecular recognition. This can be deduced from the solid-state structures, which show that the calix-shaped cavities allow an inclusion of phenyl groups

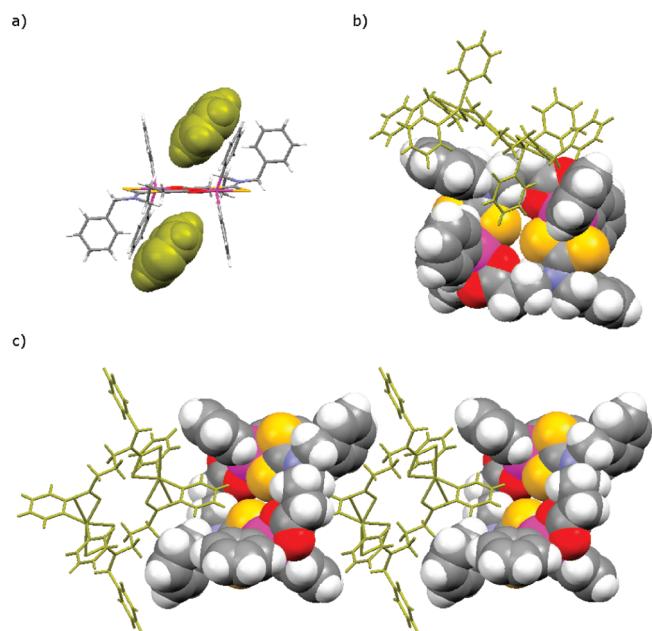


Figure 6. Fragments of the crystal lattice of compound **7** showing (a) the double-calix-shaped conformation that allows for the inclusion of phenyl groups from neighboring molecules, (b) the formation of a dimolecular supramolecular synthon, and (c) the generation of a 1D molecular arrangement.

from neighboring molecules present in the crystal lattice (Figures 6 and Figure S2, Supporting Information). Interestingly, the molecular containers are self-complementary units for the formation of a supramolecular synthon (Figure 6b) that gives rise to a 1D molecular arrangement (Figure 6c). Such supramolecular assemblies are of current interest.⁴⁷

3.3. Thermogravimetric Analysis. For the diorganotin complexes which have been obtained as solids (**1** and **3**–**7**), the thermal stability was examined by thermogravimetric analysis. While compounds **1**, **3**, and **4** start to decompose before they reach their melting point (**1**, dec. 140 °C, mp 203 °C; **3**, dec. 180 °C, mp 232 °C; **4**, dec. 120 °C, mp 156 °C), all three dinuclear macrocycles are thermally stable at least up to their melting point. While the dimethyltin derivative **5** starts to decompose upon melting (mp 192 °C), the di-*n*-butyl and diphenyltin derivatives are still stable in the liquid phase within a range of 85 °C for **6** (mp 140 °C, dec. 225 °C) and 42 °C for **7** (mp 183 °C, dec. 225 °C) before decomposition initializes.

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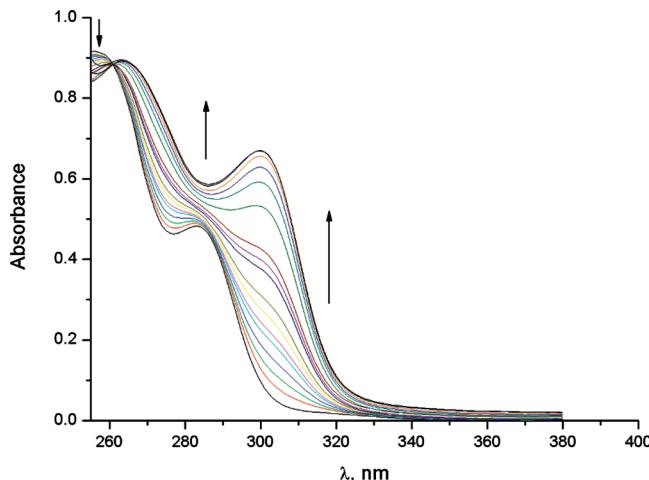


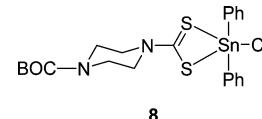
Figure 7. Changes of the absorption spectra during the titration of compound **6** (3.3×10^{-5} M) with different quantities of AcOTBA (0 to 6.9×10^{-2} M) in CHCl_3 . The arrows indicate the spectral changes occurring in response to an increasing concentration of AcOTBA.

3.4. Anion Recognition Behavior of Macrocycles **6 and **7**.** Considering that, among the compounds reported herein, macrocycles **6** and **7** should be the most appropriate hosts for anion binding, molecular recognition experiments were carried out using acetate ions (AcO^-) as guest molecules. Since the UV-vis spectra for **6** and **7** in CHCl_3 showed characteristic absorption bands (**6**, $\epsilon_{256} = 27\ 766\ \text{M}^{-1}\ \text{cm}^{-1}$, $\epsilon_{283} = 14\ 631\ \text{M}^{-1}\ \text{cm}^{-1}$; **7**, $\epsilon_{253} = 38\ 442\ \text{M}^{-1}\ \text{cm}^{-1}$, $\epsilon_{287} = 13\ 249\ \text{M}^{-1}\ \text{cm}^{-1}$) corresponding to $\pi-\pi^*$ transitions,⁴⁸ and the solutions were stable for several days at room temperature, the anion binding capacities were examined both by UV-vis and NMR titration experiments (see the Experimental Section).

Figure 7 and Figure S3 (see the Supporting Information) show the changes in the absorption spectra observed during the titration of compounds **6** and **7**, respectively, with tetrabutylammonium acetate (AcOTBA). In both cases, the maxima of the $\pi-\pi^*$ transition bands are shifted to longer wavelengths (approx. $\lambda = 300\ \text{nm}$). These bands reached saturation when a large excess of acetate salt was added; however, while for compound **7**, approximately 200 molar equivalents of the AcOTBA salt were required, for compound **6**, the bands leveled off only after approximately 1000 molar equivalents of AcOTBA had been added.

Attempts to fit the experimental titration plots (Figure S4, Supporting Information) to the formation of a 1:1 or 1:2 host–guest complex failed, indicating that a more complex process was taking place. Previous titration experiments between the mononuclear chlorodiphenyltin dithiocarbamate **8** and AcOTBA have shown that, after exchange of the chloride ion, which is completed after the addition of one molar equivalent of AcOTBA, also the dithiocarbamate ligand is displaced by AcO^- . This was evidenced by band

shifts of the $\pi-\pi^*$ transition to longer wavelengths.⁴⁹ However, there is an important difference in the complexation behavior of compounds **7** and **8**. While for the mononuclear tin dithiocarbamate **8** only approximately 10 molar equivalents of acetate are required for the dtc–acetate exchange to be quantitative, for the related macrocycle **7**, approximately 200 equivalents are necessary, indicating that the macrocycle is less prone to the decomposition.



¹H NMR titration experiments between AcOTBA and macrocycles **6** and **7** were carried out in a deuterated chloroform solution, and the resulting complexation-induced shifts for the $\text{N}-\text{CH}_2-\text{Ph}$, $\text{N}-\text{CH}_2$ -spacer, and CH_2-COO hydrogen atoms are summarized in Table 3 (entry 4 for compound **6** and entry 7 for compound **7**). The observation that the signals became broader even in the presence of less than one molar equivalent of AcOTBA, indicates that a dynamic exchange process is taking place. This is confirmed by the ¹³C NMR spectra, which gave also significant signal-broadening and highfield shifts for the tin-coordinated carboxylate and dtc groups. While the ¹¹⁹Sn NMR signals of the free macrocycle displayed narrow signals (**6**, $\delta = -230.2\ \text{ppm}$ and $\Delta\nu_{1/2} = 44\ \text{Hz}$; **7**, $\delta = -371.6\ \text{ppm}$ and $\Delta\nu_{1/2} = 22\ \text{Hz}$), these were slightly upfield-shifted and became much broader (Figure S5, Supporting Information) after the addition of a 2.3 molar excess of AcOTBA (**6**, $\delta = -231.8\ \text{ppm}$ and $\Delta\nu_{1/2} = 401\ \text{Hz}$; **7**, $\delta = -374.1\ \text{ppm}$ and $\Delta\nu_{1/2} = 269\ \text{Hz}$).

From the observed chemical shift differences in the ¹H NMR spectra, the binding constants for the 1:1 complexes were determined as $K_{\text{as}} = 15 \pm 2\ \text{M}^{-1}$ and $17 \pm 3\ \text{M}^{-1}$ for **6** and **7**, respectively (see Figure S6, Supporting Information). Evidence of binding came also from the ¹H and ¹³C NMR shift displacements of the signals corresponding to the added acetate anion. For instance, the ¹³C NMR spectra of the macrocycle–AcOTBA mixtures showed changes in the regions corresponding to the CH_3 and $\text{C}=\text{O}$ groups (Table 3, entries 4 and 7), of which the signals of the former were shifted to higher fields ($\Delta\delta = -1.314$ and $-1.366\ \text{ppm}$), whereas the signals of the latter were shifted to lower fields ($\Delta\delta = +0.659$ and $+0.197\ \text{ppm}$) when compared to the free anion in a solution of AcOTBA. Interestingly, the chemical shifts of the signals corresponding to the TBA^+ cation were also affected by the presence of macrocycles **6** and **7**, both in the ¹H and ¹³C NMR spectra (Table 3, entries 4 and 7). Thus, the ¹H NMR signals of the ³ CH_3 and ⁴ CH_2-N hydrogens of TBA^+ changed by $\Delta\delta = -0.079$ and -0.122

(48) UV-vis spectra for the unsubstituted dithiocarbamate anion and the N,N' -dimethyl dithiocarbamate anion were calculated by the time-dependent density functional theory method (TDDFT) as implemented in the Spartan 2006 software. The B3-LYP/6-31+G** approximation was employed to optimize the geometries. These calculations predicted two forbidden $n \rightarrow \pi^*$ transitions and at lower energy two $\pi \rightarrow \pi^*$ transitions polarized along different axes in the $x-y$ plane. See also: (a) Rang, K.; Sandstrom, J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 827–832. (b) Fabian, J. *Theor. Chem. Acc.* **2001**, 106, 199–217.

(49) In order to confirm the dtc-acetate exchange, a pure sample of the bis(tetrabutylammonium) dithiocarbamate salt of *N*-benzyl-4-aminopropionic acid (i.e., **L2**) was prepared, dissolved in chloroform, and examined by UV-vis spectroscopy. Since the maxima of the absorption bands fully agree with those observed during the titration experiments ($\epsilon_{264} = 15\ 100\ \text{M}^{-1}\ \text{cm}^{-1}$, $\epsilon_{300} = 15\ 800\ \text{M}^{-1}\ \text{cm}^{-1}$), it can be concluded that the dtc functions are indeed dissociated by the acetate ions from the tin coordination sphere. Thus, a large excess of AcO^- initiates decomposition of the macrocycles found in compounds **6** and **7**.

Table 3. NMR Complexation Induced Shifts (CIS) of Macrocycle **6** and **7** in the Presence of AcOTBA^a

entry	compound	¹ H and ¹³ C NMR signals of the host			¹ H and ¹³ C NMR signals of AcOTBA		
		δ (N—CH ₂ —Ph)	δ (N—CH ₂ —spacer)	δ (CH ₂ —COO)	CH ₃ COO [−]	^a CH ₂ —N	^a CH ₃
1	6 (33 mM)	4.984 (¹ H) 57.404 (¹³ C)	3.711 (¹ H) 54.459 (¹³ C)	2.224 (¹ H) 32.143 (¹³ C)			
2	AcOTBA (30 mM)				1.973 (CH ₃) 25.087 (CH ₃) 176.643 (C=O)	3.383 (¹ H) 59.075 (¹³ C)	1.005 (¹ H) 13.839 (¹³ C)
3	6 (33 mM) + AcOTBA (76 mM)	5.009 (¹ H) 57.465 (¹³ C)	3.677 (¹ H) 54.368 (¹³ C)	2.134 (¹ H) broad signal (¹³ C)	1.870 (CH ₃) 23.773 (CH ₃) 177.302 (C=O)	3.258 (¹ H) 59.074 (¹³ C)	0.926 (¹ H) 13.956 (¹³ C)
4	CIS $\Delta\delta^{b,c}$	+0.025 (¹ H) +0.061 (¹³ C)	−0.034 (¹ H) −0.091 (¹³ C)	−0.090 (¹ H)	−0.103 (CH ₃) −1.314 (CH ₃) +0.659 (C=O)	−0.122 (¹ H) −0.001 (¹³ C)	−0.079 (¹ H) +0.117 (¹³ C)
5	7 (30 mM)	4.987 (¹ H) 57.633 (¹³ C)	3.842 (¹ H) 54.658 (¹³ C)	2.315 (¹ H) 31.873 (¹³ C)			
6	7 (30 mM) + AcOTBA (70 mM)	5.019 (¹ H) broad signal (¹³ C)	3.749 (¹ H) broad signal (¹³ C)	2.232 (¹ H) broad signal (¹³ C)	1.977 (CH ₃) 23.721 (CH ₃) 176.84 (C=O) +0.004 (CH ₃) −1.366 (CH ₃) +0.197 (C=O)	3.231 (¹ H) 59.014 (¹³ C)	0.964 (¹ H) 13.945 (¹³ C) −0.152 (¹ H) −0.060 (¹³ C) +0.106 (¹³ C)
7	CIS $\Delta\delta^{b,c}$	+0.032 (¹ H)	−0.093 (¹ H)	−0.083 (¹ H)			

^a Experiments were carried out in CDCl₃ at 25 °C (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR) and are referenced to TMS (0.0 ppm for ¹H) and CDCl₃ (77.23 ppm for ¹³C). ^b Defined as $\Delta\delta = \delta(\text{signals of the mixture macrocycle} + \text{AcOTBA}) - \delta(\text{signals of } \mathbf{6} \text{ as in entry 1 or } \mathbf{7} \text{ as in entry 5 or AcOTBA 30 mM as in entry 2})$. ^c The chemical shift values for AcOTBA are dependent on the concentration of the salt; however, they displayed only minor changes (± 0.0025 ppm) within the concentration range used for the titration (10–76 mM).

ppm for **6** and $\Delta\delta = -0.041$ and -0.152 ppm for **7**, respectively. At the same time, the signals for the phenyl hydrogen atoms in the benzyl groups of macrocycles **6** and **7** were shifted in the presence of the 2.3 molar excess of AcOTBA; for example, for compound **6**, the signals for the carbon atoms in the meta and para positions were shifted upfield by $\Delta\delta = -0.243$ and -0.273 ppm, respectively. These results are indicative of a binding process taking place also for the TBA⁺ cation that involves the participation of the aromatic ligand substituent in the intermolecular interaction.

Since for steric reasons an endo coordination of the acetate anions to the tin atoms is impossible, it is proposed that the guest molecules coordinate exo to the tin atoms of compounds **6** and **7**. This is in agreement with previous studies of trinuclear macrocyclic diorganotin dicarboxylates, which have shown that Lewis bases can coordinate to the tin atoms at the periphery of the macrocycle, increasing their coordination number from six to seven, and changing the coordination geometry from skewed-trapezoidal-bipyramidal to pentagonal-bipyramidal.²⁴ According to the aromatic ring inclusion discussed above (Figure 6), at the same time, the positively charged tetrabutylammonium ions might accommodate within the macrocycle calix, thus generating an ion-pair inclusion complex (Figure 8).^{15,21}

4. Conclusions

This contribution has shown that properly designed amino acid dithiocarbamate ligands can be employed for the generation of macrocyclic assemblies having a double-calix-shaped conformation, aside from polymeric systems. Since these ligands are heteroleptic, they might be applied for the generation of mixed-metal metallosupramolecular assemblies, and systems with chiral metal centers within the macrocyclic structures. The preliminary recognition experiments with tetrabutylammonium

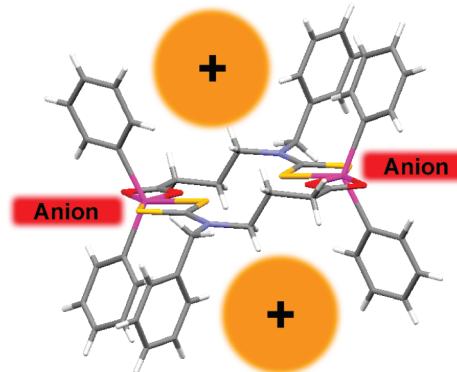


Figure 8. Representation showing how macrocycle **7** could interact simultaneously with AcO[−] anions and TBA⁺ cations (ion-pair recognition).

acetate have shown that these macrocycles might interact simultaneously with coordinating anions (AcO[−]) and organic cations (TBA⁺). Furthermore, they are self-complementary for the formation of supramolecular synthons that give rise to 1D molecular arrangements in the solid state.

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Supporting Information Available: Experimental section for the preparation of ligands **L2** and **L3**. Figure and table with calculated and experimental IR spectra for **5**. Figure showing the supramolecular interactions in the crystal structure of **6**. Additional graphics for the titration experiments. Figure of the ¹¹⁹Sn NMR spectra for **6** and **7**. Tables with atomic coordinates and selected geometric parameters for the calculated structures of **1** and **5**. Table with selected NMR data for **1**–**7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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