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Synthesis, Structural Characterization and Reactivity of (Thiolato)bismuth Complexes as Potential Water-Tolerant Lewis Acid Catalysts

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Abstract: We have synthesized bismuth complexes incorporating polydentate mono- and dithiolate ligands and examined their utility as water-tolerant Lewis acid catalysts. The reaction of $\text{Bi}(\text{OAc})_3$ or $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and the corresponding mono- or dithiol(ate) yielded the compounds $[(\text{SNNS})\text{Bi}(\text{OAc})]$ (**4**), $[(\text{SNNSPr})\text{Bi}(\text{OAc})]$ (**5**), $[(\text{NNS}_2)\text{Bi}(\text{OAc})]$ (**6**) and $[(\text{ONS}_2)\text{Bi}(\text{OAc})]$ (**7**), $[(\text{ONS}_2)\text{Bi}(\text{NO}_3)]$ (**8**) and $[(\text{NNS})_2\text{Bi}][\text{NO}_3]$ (**9**) [$\text{H}_2(\text{SNNS}) = N,N'$ -dimethyl- N,N' -bis(2-mercaptoethyl)ethylenediamine; $\text{H}_2(\text{SNNSPr}) = N,N'$ -diethyl- N,N' -bis(2-mercaptoethyl)propanediamine; $\text{H}_2(\text{NNS}_2) = N,N'$ -diethyl- N,N' -bis(2-mercaptoethyl)ethanediamine; $\text{H}_2(\text{ONS}_2) = 2$ -methoxyethyl-bis(2-mercaptoethyl)amine; $\text{H}(\text{NNS}) = N,N'$ -diethyl- N' -(2-mercaptoethyl)ethanediamine]. The solid-state structures of **4-8** show similar distorted pentagonal pyramidal geometries at the bismuth centre with a thiolate sulfur atom in the axial site, while **8** shows second structural arrangement with a distorted trigonal bipyramidal geometry at bismuth. The cation of **9** shows two NNS -bonded ligands and a distorted octahedral geometry at bismuth. Two-dimensional NMR studies of **4-8** show geminal ^1H coupling in $-\text{SCH}_2\text{CH}_2\text{N}-$ groups and suggests strong dative Bi-N intramolecular interactions. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and BiCl_3 show high activity toward the esterification of stearic acid, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and **4-7** and **9** show high activity toward the transesterification of methyl stearate in butanol, and **7** shows moderate activity as a catalyst for the transesterification of glyceryl trioctanoate in methanol.

Keywords: bismuth; thiolates; Lewis acid catalysts, transesterification, biofuels.

Introduction

A major focus in green chemistry over the past two decades has been the development of synthetic methods that involve ambient atmosphere conditions and environmentally benign solvents, such as water.¹ Central to this is the identification of catalysts that are stable under these conditions.^{2,3,4,5} Compounds of low toxicity main group metals, such as bismuth salts (e.g. chloride, bromide, acetate, triflate), have been successfully employed as useful Lewis acid catalysts for a wide variety of organic reactions, such as oxidation, reduction, C-C bond formation, protection and deprotection of functional groups, C-X (X = C, O, S, I) bond formation, rearrangements, cyclizations and ring opening reactions.^{6,7,8,9} However, these compounds are susceptible to hydrolysis and react preferentially with water rather than the substrates.^{10,11} Despite this, Bi(OH)₃ has been found to facilitate allenylation reactions in water:THF solvent mixtures, while Bi(NO₃)₃ is a useful heterogeneous catalyst for the cyclocondensation reaction of 2-aminothiophenol and aldehydes in ethanol.^{12,13} Very little work has been carried out with water-tolerant organometallic bismuth complexes, which provide possible tunability of catalytic activity through modification of organic ligands. Rare examples are the successful use of in situ generated Bi(OTf)₃ complexes of chiral ligand **1** as catalysts for aldol, asymmetric hydroxymethylation and epoxide ring-opening reactions,^{14,15,16} and the cationic organobismuth complexes **2** and **3** for allylation, epoxide ring-opening and Mannich reactions.^{17,18}

Structural Drawings of 1-3 near here

Waste greases and oils are cheap and renewable sources of triglycerides that can be converted into fatty acid methyl esters (FAME), otherwise known as biodiesel.¹⁹ Conventional transesterification processes usually involve strongly acidic or basic solutions as homogeneous catalysts.²⁰ However, free fatty acid (FFA) impurities react with basic solutions to form soaps, which makes separation of glycerol problematic.²¹ Further, the presence of water leads to hydrolysis of oils and FAME in the presence of strong acids and bases.²² Therefore, ideal homogeneous catalysts for biodiesel production from waste oils must catalyze esterification reactions of carboxylic acids (fatty acids) with alcohol, as well as transesterification reactions of triglycerides.²³ Lewis acidic tin, lead, mercury and zinc complexes of have been studied for their ability to facilitate these reactions, with tin compounds showing the most promising results.^{20,24,25}

We have previously reported that indium thiolate compounds incorporating (SOOS)²⁻, (SNNS)²⁻, (SNNSPr)²⁻ and (NNS₂)²⁻ ligands [$\text{H}_2(\text{SOOS}) = 2,2\text{-(ethylenedioxy)diethanethiol}$, $\text{H}_2(\text{SNNS}) = N,N'\text{-dimethyl-}N,N'\text{-bis(2-mercaptoethyl)ethylenediamine}$; $\text{H}_2(\text{SNNSPr}) = N,N'\text{-diethyl-}N,N'\text{-bis(2-mercaptoethyl)propanediamine}$; $\text{H}_2(\text{NNS}_2) = N,N\text{-diethyl-}N',N'\text{-bis(2-mercaptoethyl)ethanediamine}$] are moderately efficient Lewis acid catalysts toward esterification/transesterification reactions in the presence of water.²⁶ Polydentate thiolate ligands afford metal-sulfur bonds that are stable to hydrolysis for soft main group metals, while secondary donor atoms affect the coordination environment, Lewis acidity and reactivity of the metal centre.^{27,28} We now report the synthesis and characterization of a series of (thiolato)bismuth compounds (**4-9**), and their ability to perform as water-tolerant Lewis acid catalysts for esterification and transesterification reactions of fatty acids and fatty acid esters, respectively.

Structural Drawings of proligands and 4-9 near here

Experimental

General

Solution ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 23°C on either a JEOL 400 SS spectrometer (400 and 100 MHz, respectively), or a Varian Mercury 200 MHz + spectrometer (200 and 50 MHz, respectively), and chemical shifts are calibrated to the residual solvent signal. ATR FT-IR spectra were recorded on a Thermo Nicolet iS5 FT-IR spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$. FT-Raman spectra were recorded on a Thermo Nicolet NXR 9600 Series FT-Raman spectrometer in the range $3900\text{--}70\text{ cm}^{-1}$. Melting points were recorded on an Electrothermal MEL-TEMP melting point apparatus and are uncorrected. Elemental analyses were performed by Laboratoire d'analyse élémentaire, Université de Montréal, Montreal, Canada.

N,N'-dimethylethylenediamine (85%), *N,N'*-diethyl-1,3-propanediamine (97%), *N,N'*-diethylethylenediamine (99%), 2-methoxyethylamine (95%), ethylene sulfide (98%), stearic acid (98.5%), methyl stearate (99%) and glyceryl trioctanoate ($\geq 99\%$) were used as received from Sigma-Aldrich. Potassium hydroxide pellets (97.0%) were used as received from Caledon. Bismuth(III) acetate ($\geq 99.99\%$) was used as received from Alfa Aesar. Bismuth(III) nitrate pentahydrate (98.0%) was used as received from Fisher Scientific. $\text{H}_2(\text{SNNS})$, $\text{H}_2(\text{SNNSPr})$,²⁹ $\text{H}_2(\text{NNS}_2)$, $\text{H}(\text{NNS})$,³⁰ and $\text{H}_2(\text{ONS}_2)$ ³¹ were prepared according to literature methods.

Synthesis

Synthesis of [(SNNS)Bi(OAc)] (4)

Under a stream of dinitrogen, Bi(OAc)₃ (0.463 g, 1.12 mmol) was added to a solution of H₂(SNNS) (0.250 g, 1.12 mmol) in 95% ethanol (10 mL) to yield a yellow solution immediately. After stirring for 3 h, the colourless precipitate was filtered. The yellow filtrate was then concentrated to 1 mL and allowed to sit at 4 °C for 5 d to afford crystals of **4** (0.313 g, 0.660 mmol 55%). Anal. Calc. for C₁₀H₂₁BiN₂O₂S₂: C, 25.32; H, 4.46; N, 5.91; S, 13.52. Found: C, 25.31; H, 4.44; N, 5.94; S, 14.07. M.p. 227-229°C (d). FT-IR(cm⁻¹): 619 m, 658 vs, 740 s, 756 s, 879 m, 917 m, 951 s, 1005 m, 1020 m, 1038 m, 1050 m, 1087 m, 1130 m, 1168 m, 1198 m, 1215 m, 1259 m, 1280 s, 1308 m, 1334 s, 1378 vs, 1397s, 1421 m, 1446 m, 1557 vs, 2832 m, 2862 m, 2951 w. FT-Raman (cm⁻¹): 115 m, 142 m, 159 m, 181 m, 277 vs, 295 vs, 316 m, 343 m, 435 w, 472 w, 669 w, 760 vw, 923 w, 1005 vw, 1131 w, 1276 vw, 1300 vw, 1366 vw, 1426 w, 1561 vw, 2831 w, 2863 w, 2908 w, 2943 w. ¹H NMR (CDCl₃, ppm): 1.97 (s, O₂CCH₃, 3H), 2.44 (s, NCH₃, 6H), 2.77-2.84 (m, N(CH₂)₂NCH₃, 4H), 2.88-2.95 (m, NCH_aCH₂S, 2H), 3.43-3.50 (m, NCH₂CH_aS, 2H), 3.54-3.57 (m, NCH_bCH₂S, 2H), 4.63-4.68 (m, NCH₂CH_bS, 2H). ¹³C{¹H} NMR (CDCl₃, ppm): 23.8 (O₂CCH₃), 26.7 (SCH₂), 41.35 (NCH₃), 56.4 (N(CH₂)₂N), 64.7 (NCH₂CH₂S), 180.9 (O₂CCH₃).

Synthesis of [(SNNSPr)Bi(OAc)] (5)

Under a stream of dinitrogen, Bi(OAc)₃ (0.385 g, 0.998 mmol) was added to a solution of H₂(SNNSPr) (0.250 g, 0.998 mmol) in 95% ethanol (10 mL) to yield a yellow solution immediately. After stirring for 3 hours, the reaction was filtered. The yellow filtrate was then concentrated to 1.5 mL, layered with diethyl ether (4.5 mL) and allowed to sit at 4 °C for 10 d to

afford crystals of **5** (0.258 g, 0.500 mmol, 50%). Anal. Calc. for $C_{13}H_{27}BiN_2O_2S_2$: C, 30.23; H, 5.27; N, 5.42; S, 12.42. Found: C, 30.13; H, 5.25; N, 5.46; S, 12.90. M.p. 173-175°C (d). FT-IR(cm^{-1}): 559, w, 615 m, 654 vs, 705 m, 740 s, 786 w, 838 w, 872 w, 921 m, 972 s, 993 m, 1019 m, 1045 m, 1059 m, 1091 m, 1110 m, 1123 m, 1154 m, 1175 w, 1199 m, 1213 m, 1230 m, 1254 w, 1281 m, 1313 m, 1328 s, 1376 vs, 1443 m, 1473 m, 1563 s, 2914 w, 2980 s. FT-Raman (cm^{-1}): 118 m, 139 m, 157 m, 175 m, 203 m, 247 m, 282 s, 305 vs, 369 w, 470 w, 534 w, 506 w, 654 w, 891 vw, 922 w, 976 vw, 1022 vw, 1061 w, 1093 w, 1112 w, 1232 vw, 1290 vw, 1333 vw, 1379 vw, 1448 w, 1471 w, 1567 vw, 2848 w, 2916 m, 2935 m, 2968 w. ^1H NMR ($CDCl_3$, ppm): 0.99 (t, NCH_2CH_3 , 6H), 1.77 (br, $NCH_2CH_2CH_2N$, 2H), 1.98 (s, O_2CCH_3 , 3H), 2.78-3.37 (m, NCH_2 , 12H), 3.67 (br, SCH_a , 2H), 4.40 (br, SCH_b , 2H). ^{13}C { ^1H } NMR ($CDCl_3$, ppm): 7.61 (NCH_2CH_3), 21.9 ($NCH_2CH_2CH_2N$), 23.5 (O_2CCH_3), 26.2 (SCH_2), 44.8 (NCH_2CH_3), 52.3 ($NCH_2CH_2CH_2N$), 59.5 (NCH_2CH_2S), 179.9 (O_2CCH_3).

Synthesis of [(NNS₂)Bi(OAc)] (6)

Under a stream of dinitrogen, $Bi(OAc)_3$ (0.408 g, 1.06 mmol) was added to a solution of $H_2(NNS_2)$ (0.250 g, 1.06 mmol) in 95% ethanol (10 mL) to yield a yellow solution immediately. After stirring for 3 hours, the reaction was filtered. The yellow filtrate was then concentrated to 2 mL, layered with diethyl ether (4.5 mL) and allowed to sit at 4 °C for 3 d to afford crystals **6** (0.269 g, 0.535 mmol, 51%). Anal. Calc. for $C_{12}H_{25}BiN_2O_2S_2$: C, 28.70; H, 5.02; N, 5.58; S, 12.80. Found: C, 28.75; H, 5.05; N, 5.52; S, 12.93. M.p. 184-186°C. FT-IR(cm^{-1}): 618 m, 658 vs, 720 m, 736 m, 778 m, 841 m, 883 m, 925 m, 941 m, 992 m, 1013 m, 1054 m, 1089 m, 1139 m, 1163 m, 1193 m, 1209 w, 1246 m, 1279 m, 1315 s, 1332 s, 1374 vs, 1393 s, 1436 m, 1457 m, 1558 m, 2905 m, 2980 m. FT-Raman (cm^{-1}): 137 s, 184 m, 259 s, 291 vs, 328 s, 419 vw, 464 vw,

495 w, 665 w, 735 vw, 897 vw, 925 w, 992 vw, 1054 vw, 1106 vw, 1136 vw, 1244 vw, 1278 vw, 1318 vw, 1374 vw, 1459 w, 1564 vw, 2857 m, 2908 m, 2927 m. ^1H NMR (CDCl_3 , ppm): 1.06 (t, NCH_2CH_3 , 6H), 1.96 (s, O_2CCH_3 , 3H), 2.70-2.83 (m, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$, 8H), 2.94-3.00 (m, $\text{NCH}_a\text{CH}_2\text{S}$, 2H), 3.36-3.41 (m, $\text{NCH}_b\text{CH}_2\text{S}$, 2H), 3.91-3.98 (m, $\text{NCH}_2\text{CH}_a\text{S}$, 2H), 4.46-4.52 (m, $\text{NCH}_2\text{CH}_b\text{S}$, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 9.7 (NCH_2CH_3), 23.5 (O_2CCH_3), 28.0 (SCH_2), 45.5 (NCH_2CH_3), 49.5 ($\text{NCH}_2\text{CH}_2\text{NEt}_2$), 57.1 ($\text{NCH}_2\text{CH}_2\text{NEt}_2$), 65.9 ($\text{NCH}_2\text{CH}_2\text{S}$), 180.38 (O_2CCH_3).

Synthesis of $[(\text{ONS}_2)\text{Bi}(\text{OAc})]$ (7)

Under a stream of dinitrogen, $\text{Bi}(\text{OAc})_3$ (0.494 g, 1.28 mmol) was added to a clear colorless solution of $\text{H}_2(\text{ONS}_2)$ (0.250 g, 1.28 mmol) in 95% ethanol (10 mL) to yield a yellow solution immediately. After stirring for 3 hours, the reaction was filtered. The yellow filtrate was allowed to sit at 4 °C for 2 d to afford crystals of **7** (0.247 g, 0.535 mmol, 42%). Anal. Calc. for $\text{C}_9\text{H}_{18}\text{BiNO}_3\text{S}_2$: C, 23.43; H, 3.93; N, 3.04; S, 13.90. Found: C, 23.33; H, 3.90; N, 3.07; S, 13.80. M.p. 183-185°C. FT-IR(cm^{-1}): 619 m, 662 vs, 721 m, 834 s, 891 m, 923 m, 964 m, 983 m, 1006 s, 1018 s, 1082 s, 1103 s, 1126 m, 1181 w, 1194 w, 1238 w, 1261 m, 1333 s, 1375 s, 1398 m, 1445 m, 1557 m, 2839 m, 2917 m. FT-Raman (cm^{-1}): 131 m, 169 m, 210 w, 271 m, 297 s, 340 m, 377 w, 426 vw, 471 vw, 486 vw, 665 w, 722 vw, 836 vw, 887 vw, 927 w, 1019 vw, 1079 vw, 1129 vw, 1201 vw, 1244 vw, 1286 vw, 1379 vw, 1451 w, 1564 vw, 2848 w, 2917 m. ^1H NMR (CDCl_3 , ppm): 1.96 (s, O_2CCH_3 , 3H), 2.91 (t, OCH_2 , 2H), 3.00-3.07 (m, $\text{NCH}_a\text{CH}_2\text{S}$, 2H), 3.23-3.31 (m, $\text{NCH}_b\text{CH}_2\text{S}$, 2H), 3.44 (s, OCH_3 , 3H), 3.55 (t, $\text{NCH}_2\text{CH}_2\text{O}$, 2H), 3.99-4.05 (m, SCH_a , 2H), 4.30-4.36 (m, SCH_b , 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 23.3 (O_2CCH_3), 27.5 (SCH_2), 58.7 (OCH_3), 59.0 (OCH_2), 64.9 ($\text{NCH}_2\text{CH}_2\text{S}$), 67.2 ($\text{NCH}_2\text{CH}_2\text{O}$), 180.0 (O_2CCH_3).

Synthesis of [(ONS)₂Bi(NO₃)] (8)

Under a stream of dinitrogen, H₂(ONS₂) (0.250 g, 1.28 mmol) was added to a solution of potassium hydroxide (0.144 g, 2.56 mmol) in acetone (10 mL), followed by addition of Bi(NO₃)₃·5H₂O (0.621 g, 1.28 mmol). After stirring for 3 h, the reaction mixture was filtered to afford a pale yellow solution. The filtrate was concentrated to 1 mL and allowed to sit at 23 °C for 2 days to afford crystals of **8** (0.087g, 0.19 mmol 15%). Anal. Calc. for C₇H₁₅BiN₂O₄S₂: C, 18.11; H, 3.26; N, 6.03; S, 13.81. Found: C, 18.21; H, 2.99; N, 6.13; S, 13.62. M.p. 138°C. FT-IR (cm⁻¹): 668 w, 718 m, 808 m, 838 w, 885 vw, 915 vw, 942 vw, 967 vw, 1014 m, 1066 w, 1105 m, 1266 s, 1417 m, 2359 vw, 2927 vw. FT-Raman (cm⁻¹): 131 m, 174 m, 298 s, 348 m, 393 vw, 505 vw, 669 w, 1028 w, 1446 w, 2928 m. ¹H NMR (dmso-*d*₆, ppm): 3.13 (t, OCH₂, 2H), 3.19-3.27 (m, NCH_aCH₂S, 2H), 3.36 (s, OCH₃, 3H), 3.51 (t, NCH₂CH₂O, 2H), 3.90-3.98 (m, NCH_bCH_aS, 4H), 4.69-4.71 (m, SCH_b, 2H). ¹³C{¹H} NMR (dmso-*d*₆, ppm): 29.2 (SCH₂), 58.6 (OCH₃), 58.8 (OCH₂), 66.3 (NCH₂CH₂S), 66.9 (NCH₂CH₂O).

Synthesis of [(NNS)₂Bi][NO₃] (9)

Under a stream of dinitrogen, H(NNS) (0.250 g, 1.42 mmol) was added to a solution of potassium hydroxide (0.080 g, 1.4 mmol) in acetone (10 mL), followed by addition of Bi(NO₃)₃·5H₂O (0.344 g, 0.709 mmol). After stirring for 3 h, the reaction mixture was filtered to afford a pale yellow solution. The filtrate was then allowed to sit at -15 °C for 2 days to afford crystals of **9** (0.239 g, 0.367 mmol, 52%). Anal. Calc. for C₃₅H₈₂Bi₂N₁₀O₇S₄: C, 32.30; H, 6.35; N, 10.76; S, 9.86. Found: C, 31.49; H, 6.30; N, 10.76; S, 10.49. M.p. 106°C. FT-IR (cm⁻¹): 571 m, 663 m, 707 w, 733 s, 787 vw, 812 m, 910 w, 957 w, 985 vw, 1006 m, 1030 s, 1050 vw, 1062 vw, 1099 w, 1148 m, 1191 m, 1220 m, 1264 m, 1329 vs, 1361 s, 1442 m, 1466 w, 1495 w, 2816

m, 2966 m, 3162 m. FT-Raman (cm^{-1}): 130 s, 188 m, 263 s, 333 vs, 666 vw, 734 vw, 908 vw, 1043 m, 1125 vw, 1220 vw, 1284 vw, 1374 vw, 1446 w, 2858 w, 2922 m. ^1H NMR (CDCl_3 , ppm): 0.95-1.00 (m, NCH_2CH_3 , 12H), 1.69-5.79 (m, 26H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 10.0 (NCH_2CH_3), 27.9 (SCH_2), 45.7 (NCH_2CH_3), 48.6 ($\text{NCH}_2\text{CH}_2\text{NEt}_2$), 51.8 ($\text{NCH}_2\text{CH}_2\text{NEt}_2$), 58.5 ($\text{NCH}_2\text{CH}_2\text{S}$).

Catalysis experiments

Esterification of stearic acid

To a solution of stearic acid (0.100 g, 0.352 mmol) in MeOH (1 mL, 0.792 g, 24.7 mmol) was added 10 mol% of the bismuth precatalyst (0.035 mmol). The resulting solution was heated to reflux for 4 h, after which the excess methanol was removed under reduced pressure. The residue was extracted with diethyl ether and the solvent was removed under vacuum to yield the crude product. Samples were analyzed by ^1H NMR spectroscopy in CDCl_3 to determine conversion of stearic acid to methyl stearate.

Transesterification of methyl stearate

Methyl stearate (0.100 g, 0.335 mmol) was dissolved in 1-butanol (1 mL, 0.810 g, 10.9 mmol) with subsequent addition of 10 mol% of the bismuth precatalyst (0.035 mmol). The resulting solution was heated at reflux for 19 h, after which the solvent was removed under vacuum. The residue was extracted with diethyl ether (5 mL) and the solution washed with distilled water (5 mL). The organic layer was then dried over anhydrous sodium sulfate and the

solvent removed under vacuum to yield the crude product. Samples were analyzed by ^1H NMR spectroscopy in CDCl_3 to determine conversion of methyl stearate to 1-butyl stearate.

Transesterification of glyceryl trioctanoate

Glyceryl trioctanoate (0.150 g, 0.319 mmol) was dissolved in MeOH (1 mL, 0.792 g, 24.7 mmol) with subsequent addition of 10 mol% of the bismuth precatalyst (0.032 mmol). The resulting solution was refluxed for 19 h, after which excess alcohol was removed under vacuum. The residue was extracted with diethyl ether (5 mL), washed with distilled water (5 mL), dried over anhydrous sodium sulfate, and the solvent removed under vacuum to yield the crude product. Samples were analyzed by ^1H NMR spectroscopy in CDCl_3 to determine conversion of glyceryl trioctanoate to methyl stearate.

X-ray crystallography

Crystals of **4-9** were isolated from the reaction mixtures as indicated above. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT)³² and corrected for absorption (SADABS).³³ The structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL).³⁴ All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model. Crystallographic data are given in Table 1.

For **7**, the thiol ligand was disordered and the site occupancies determined using an isotropic model as 0.6 [S(1), N(1), C(1)-C(2)] and 0.4 [S(1a), N(1a), C(1a)-C(2a)] and fixed in subsequent refinement cycles. Bond distances within the disordered moiety were restrained to similar values and thermal parameters of atoms in close proximity were constrained to equal values. Data were collected at room temperature. All attempts at collecting data at low temperatures failed and led to poor data quality. For **9**, one of C₂ units of one of the ligands was disordered over two positions and the site occupancy determined using an isotropic model as 0.56 (C(9)-C(10)) and 0.44 (C(9A)-C(10A)) and fixed in subsequent refinement cycles. Atoms in close proximity had thermal parameters constraint to identical values. The acetone molecule was disordered and could not be modelled properly. The solvent molecule was modelled using disordered electron densities (SQUEEZE).³⁵

Computational methods

DFT calculations were performed using Gaussian 09 at the B3LYP 6-31G* level of theory for all atoms except Bi, for which Stuttgart electron core pseudo-potentials (sdd) were employed.³⁶ All structures were geometry optimized and structural parameters for input files were derived from crystal structure data where possible. Frequency calculations were performed on all structures and gave no imaginary frequencies. Structural parameters are given in the Supplementary material.

Results and discussion

Synthesis

Compounds **4-7** were prepared via the metathesis reaction of bismuth acetate and one equivalent of the corresponding dithiol in 95% ethanol. Compound **8** was prepared via the deprotonation of $\text{H}_2(\text{ONS}_2)$ with two equivalents of KOH in acetone, followed by addition of one equivalent of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Compound **9** was prepared in a similar manner, but required two equivalents of the monothiol $\text{H}(\text{NNS})$. Reactions were stirred at 23°C for 3 h, filtered, and the product crystallized from the reaction filtrate in moderate yield (42-55 %), with the exception of **8** which was isolated in low yield (15%). The latter may be the result of an undesirable KOH catalyzed aldol condensation reaction of the acetone solvent.

X-ray crystal structures

Crystals suitable for X-ray crystallographic analysis were isolated from the corresponding reaction mixtures at 4°C (**4-7**), 23°C (**8**) or -15°C (**9**). Selected bond distances and angles are given in Tables 2 and 3.

The structure of $[(\text{SNNS})\text{Bi}(\text{OAc})]$ (**4**) (Figure 1) shows bismuth bonded to a tetradentate (SNNS) ligand and a chelating acetate- $\kappa^2\text{O},\text{O}'$ group. The geometry at the metal centre is distorted pentagonal pyramidal, with a thiolate sulfur atom (S2) in the axial position and a thiolate sulfur atom, two amine nitrogen atoms and two acetate oxygen atoms in equatorial positions. The open coordination site is occupied by a stereochemically active valence lone pair of electrons (*vide infra*). The Bi-S_{eq} bond distance [$\text{Bi1-S1} = 2.577(2) \text{ \AA}$] is much larger than the Bi-S_{ax} bond distance [$\text{Bi1-S2} = 2.529(2) \text{ \AA}$], as a result of the trans influence of the amine nitrogen atom N2 [$\text{S1-Bi1-N2} = 140.9(1)^\circ$]. Also, the Bi1-N2 bond distance [$2.786(5) \text{ \AA}$] is much larger than Bi1-N1 [$2.564(6) \text{ \AA}$], as a result of stronger trans influence of the thiolate

versus the acetate group [$\text{N1-Bi1-C9} = 173.3(2)^\circ$]. Finally, the acetate group is bonded asymmetrically to the bismuth centre [$\text{Bi1-O1} = 2.874(6)$, $\text{Bi1-O2} = 2.375(4)$ Å].

The structure of $[(\text{SNNSPr})\text{Bi}(\text{OAc})]$ (**5**) (Figure 2) is similar to that of **4**. The most significant structural differences in **5** are a larger N1-Bi1-N2 ligand bite angle [**4**: $67.8(2)^\circ$, **5**: $77.9(1)^\circ$], due to the propylene ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$) versus ethylene ($\text{NCH}_2\text{CH}_2\text{N}$) linkage, and a larger S1-Bi1-S2 angle [**4**: $88.51(6)^\circ$, **5**: $99.02(5)^\circ$]. Further, corresponding Bi-N bond distances [$\text{Bi1-N1} = 2.607(4)$ and $\text{Bi1-N2} = 2.901(5)$ Å] are larger than in **4**, as is the Bi1-O1 bond distance [**4**: $2.874(6)$ Å, **5**: $2.921(6)$ Å]. However, no resultant shortening of the Bi-S bonds is observed in **5**.

The structure of $[(\text{NNS}_2)\text{Bi}(\text{OAc})]$ (**6**) (Figure 3) shows bismuth bonded to a tetradentate (NNS_2) ligand and a chelating acetate- $\kappa^2\text{O},\text{O}'$ group. The geometry at the metal centre is distorted pentagonal pyramidal, with a thiolate sulfur atom (S2) in the axial position and a thiolate sulfur atom, two amine nitrogen atoms and two acetate atoms in equatorial positions. The open coordination site is occupied by a stereochemically active valence lone pair of electrons. Overall, the bonding environment at bismuth resembles that of compounds **4** and **5**. Despite the change in connectivity of the ligand donor atoms in (NNS_2) versus (SNNS), the structural parameters for **6** are very similar to that of **4**. However, the S2-Bi1-N1 angle [$75.5(1)^\circ$] in **6** is more acute as a result of tethering of S2 and N1 by a $-\text{CH}_2\text{CH}_2-$ linkage as compared to **4** and **5**, while the absence of a $-\text{CH}_2\text{CH}_2-$ linkage between S2 and N2 results in a more obtuse S2-Bi1-N2 [$85.75(9)^\circ$] angle. This affects a larger S1-Bi1-S2 angle [$96.02(5)^\circ$], larger equatorial Bi1-S1 [$2.613(2)$ Å] and Bi1-N2 [$2.919(5)$ Å] bond distances, and a corresponding decrease in the Bi1-O1 bond distance [**4**: $2.874(6)$ Å, **5**: $2.725(5)$ Å].

The structure of $[(\text{ONS}_2)\text{Bi}(\text{OAc})]$ (**7**) (Figure 4) is similar to that of **6**, except that the ligand NEt_2 group is replaced with an $-\text{OMe}$ group. The most significant structural differences in **7** are shorter Bi-S, Bi-N and Bi- $\text{O}_{\text{acetate}}$ bond distances. This is presumably a result of the weaker donor ability of the ether oxygen in (ONS_2) versus the amine nitrogen in (NNS_2) .

The structure of $[(\text{ONS}_2)\text{Bi}(\text{NO}_3)]$ (**8**) (Figure 5) contains four unique molecules in the asymmetric unit, and two different bonding environments at bismuth (see Table S1). The metal bonding environment at Bi1/3 is similar to that of **7** with the most significant structural differences being the longer Bi- $\text{O}_{\text{nitrate}}$ bond distances in **8** [Bi1-O1 = 2.778(12) and Bi1-O2 = 2.498(9) Å] versus the Bi- $\text{O}_{\text{acetate}}$ bond distances in **7** [Bi1-O1 = 2.709(6) and Bi1-O2 = 2.332(4) Å]. However, this is not accompanied by a decrease in Bi-S/N/ O_{ligand} bond distances in **8**. Unlike Bi1/3, the metal bonding environments at Bi2/4 show similar Bi-S bond distances [Bi1-S1 = 2.573(3) and Bi1-S2 = 2.528(3) Å; Bi2-S3 = 2.547(3) and Bi2-S4 = 2.547(3) Å]. There is also a shorter Bi- O_{Me} bond at Bi2/4 [Bi1-O3 = 2.826(10) Å; Bi2-O8 = 2.770(8) Å] and a longer secondary Bi- O_{NO_3} interaction [Bi1-O2 = 2.778(12) Å; Bi2-O6 = 3.031(10) Å]. This is accompanied by a significant increase in the $\text{S}_{\text{apical}}\text{-Bi-O}_{\text{Me}}$ bond angle [$\text{S2-Bi1-O3} = 87.7(2)^\circ$; $\text{S4-Bi2-O8} = 134.4(2)^\circ$]. The geometry at Bi2/4 may be most accurately described as distorted trigonal bipyramidal if the nitrate group is considered to occupy a single coordination site [$\text{N3-Bi2-N4} = 160.9(4)^\circ$; $\text{S3-Bi2-S4} = 101.04(10)^\circ$, $\text{S3-Bi2-O8} = 100.5(3)^\circ$ and $\text{S4-Bi2-O8} = 134.4(2)^\circ$].

The solid-state structures of **4-7** and **8** (Bi1/3) are similar to observed to that of tris(aminoethanethiolato)bismuth $[(\text{H}_2\text{NCH}_2\text{CH}_2\text{S})_3\text{Bi}]$, reported previously.³⁷ All feature a distorted pentagonal pyramidal structure and an apical thiolate sulfur atom. These are also

reminiscent of distorted square pyramidal structure of $[(\text{Me}_2\text{NCH}_2\text{CH}_2\text{S})_2\text{BiCl}]$, which possesses a monodentate chloride versus bidentate acetate group.³⁷

The structure of **9** (Figure 6) shows a monomeric unit in which two of the NNS ligands chelate the bismuth center in an *NNS* manner. The nitrate group is not coordinated to the bismuth centre [$\text{Bi1-O1} = 3.616(5) \text{ \AA}$; sum of ionic radii = $2.43 \text{ \AA}$; sum of van der Waals radii = $3.80 \text{ \AA}$],³⁸ and the bismuth complex is therefore cationic. The bismuth centre is six-coordinate and has a distorted octahedral geometry [$\text{S1-Bi1-N2} = 143.77(8)^\circ$; $\text{S2-Bi1-N4} = 141.38(9)^\circ$; $\text{N1-Bi1-N3} = 152.26(12)^\circ$]. This deviation from ideal bond angles is due to the constraints imposed by the ligand backbone and a stereochemically active lone pair. The Bi1-N2 and Bi1-N4 bond distances [$2.972(4)$ and $3.005(4) \text{ \AA}$, respectively] are significantly longer than the Bi1-N1 and Bi1-N3 bond distances [$2.488(4)$ and $2.527(5) \text{ \AA}$, respectively]. Further, the sulfur atoms are in *cis* positions [$\text{S1-Bi1-S2} = 93.71(5)^\circ$] and the two central N-H ligand nitrogen atoms [N2 and N4] are in orthogonal *trans* positions. Therefore, the structure appears to have a core ψ -trigonal bipyramidal structure with the two thiolate sulfur atoms and a stereochemically active lone pair in the equatorial sites, and the two N-H nitrogen atoms occupying axial sites. This arrangement mimics the structures of the bis(aminoethanethiolato)bismuth nitrate compounds $[(\text{H}_2\text{NCH}_2\text{CH}_2\text{S})_2\text{Bi}(\text{NO}_3)]$ and $[(\text{H}_2\text{NCH}_2\text{CH}_2\text{S})_2\text{Bi}(\text{NO}_3)(\text{H}_2\text{O})]$.^{37,39} The terminal $-\text{NEt}_2$ amine groups are weakly coordinated to the open face of the structure containing the lone pair of electrons (*vide infra*).

DFT computational studies

DFT calculations were performed to rationalize the observed solid-state structures and

probe bonding at bismuth. Structural parameters for geometry optimized [(SNNS)Bi(OAc)] are similar to those of **4** in the solid-state (Table S2), though Bi-O_{acetate} bond distances are short [Bi1-O1 = 2.31 vs. 2.375(4) Å; Bi1-O2 = 2.66 vs. 2.874(6) Å]. Analysis of molecular orbitals shows that HOMO, HOMO-1 and HOMO-2 (Figure 7) are primarily thiolate sulfur lone pairs with electron density in the position trans to the axial Bi1-S2 bond, i.e. in the assumed position of the stereochemically active lone pair of electrons on bismuth. The geometry optimized structure of [(NH₃)₂(MeS)₂Bi(OAc)], which features untethered amine and thiolate groups, shows a distorted pentagonal pyramidal bonding environment at bismuth (Table S3) similar to that observed for the solid-state structures of **4-6**. This suggests that this is the most favourable structural arrangement and tethering of the amine nitrogen atoms, and thiolate sulfur atoms via -CH_n- (n = 2, 3) linkages causes minimal distortion of the bismuth bonding environment. Structural parameters for geometry optimized [(ONS₂)Bi(NO₃)] are similar to those of the two unique bonding environments of **8** in the solid-state (Table S4), though Bi-O_{nitrate} bond distances are short [Bi1-O1 = 2.32 vs. 2.375(4) Å; Bi1-O2 = 2.62 vs. 2.874(6) Å; Bi2-O5 = 2.29 vs. 2.514(8) Å; Bi2-O6 = 2.74 vs. 3.031(10) Å]. The structure of the Bi2 molecule was calculated to be 8 kJ mol⁻¹ lower in energy than that of the Bi1 molecule. The observation of both structural arrangements in the solid-state is presumably a result of packing forces. Finally, geometry optimization of [(H₂NCH₂CH₂S)₂Bi]⁺ shows a similar ψ-trigonal bipyramidal N₂S₂ bonding environment and structural parameters at bismuth as the core structure of **9** (Table S5), suggesting very weak bonding interactions from the ligand -NEt₂ groups.

Solution NMR Characterization

^1H NMR spectra of **4-8** show that the protons of the two $-\text{SCH}_2\text{CH}_2\text{N}-$ units within each of the ligands (SNNS), (SNNSPr), (NNS₂) and (ONS₂) are chemically equivalent, suggesting that the observed chiral solid-state pentagonal pyramidal structures are fluxional and not retained in solution. This is further supported by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, which show a single set of $\text{SCH}_2\text{CH}_2\text{N}$ resonances for each compound. Despite this, geminal coupling of the methylene protons within each $\text{SCH}_2\text{CH}_2\text{N}$ unit is observed (see Figures S1-S5). In the ^1H NMR spectrum of compound **7**, for example, the magnetically inequivalent SCH_2 protons display an overlapping doublet of triplets (H_a) and doublet of doublets (H_b) splitting pattern (Figure 8a). The coupling pattern expected for H_a from the Newman projection of **7** (Figure 8b) suggests that the coupling of H_a to H_b , followed by equal coupling to H_c/H_d will give rise to a doublet of triplets pattern. This will occur if the dihedral angle of H_a to H_c and H_d equals approximately 60° , which is the case for the calculated positions of the corresponding hydrogen atoms in the X-ray crystal structure of **7**. Alternatively, the coupling pattern of H_b arises from the geminal coupling of H_b to H_a , followed by unequal coupling to H_c and H_d . The latter results from the differing dihedral angles of H_b to H_c (180°) and H_d (60°).

These assignments are confirmed by the COSY ^1H NMR spectrum of compound **7** (Figure 9a), which shows coupling among the multiplets at 3.00-3.07, 3.23-3.31, 3.99-4.05 and 4.30-4.36 ppm. The corresponding HSQC spectrum (Figure 9b) confirms that the peaks at 3.99-4.05 and 4.30-4.36 ppm are bonded to the same carbon atom (27.5 ppm, SCH_2), and those at 3.00-3.07, 3.23-3.31 ppm are bonded to the same carbon atom (64.9 ppm, NCH_2). Similar coupling patterns are observed for the $-\text{SCH}_2\text{CH}_2\text{N}-$ groups in the ^1H NMR spectra of **4-6** and **8**, though peak broadening in **5** obscures the $^3J(^1\text{H}-^1\text{H})$ coupling. This is presumably a result of increased ligand (Bi-N) lability afforded by the $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}-$ backbone. Alternatively, no

geminal coupling is observed for the $\text{-OCH}_2\text{CH}_2\text{N-}$ protons in **7** or **8**, as demonstrated by the triplets at 2.91 (OCH_2) and 3.55 ppm (CH_2N) in **7**, or the $\text{-NCH}_2\text{CH}_2\text{N-}$ / $\text{-NCH}_2\text{CH}_2\text{CH}_2\text{N-}$ protons in **4-6**.

The ^1H NMR spectrum of **9** in CDCl_3 at 23°C shows very broad peaks, which is presumably a result of weak $\text{Bi-N}_{\text{Et}_2}$ bonding interactions, as observed in the X-ray crystal structure, and fluxional behavior in solution. Peaks are better resolved at -50°C and complex second order patterns suggest the presence of geminal coupling. However, decreased solubility of the compound at lower temperatures precludes the collection of HSQC data and peak assignments are not possible.

Esterification and transesterification reactions

The esterification of stearic acid to methyl stearate was carried out in refluxing methanol for 4 hours using bismuth salts and compounds **4-9** as catalysts (Table 4). BiCl_3 and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ gave near quantitative yields, respectively. Of the bismuth (di)thiolate compounds, compound **8** gave a low yield (22%), while trace amounts of product were found for **4-7** and **9**.

The transesterification of methyl stearate to butyl stearate was carried out in refluxing *n*-butanol for 19 hours using bismuth salts and compounds **4-9** as catalysts (Table 5). Both BiCl_3 and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ gave high yields, with the latter near quantitative. Bismuth thiolate compounds **4-9** also gave high yields (79-100%), with the exception of compound **5** which gave a yield of 25%.

Finally, the transesterification of glyceryl trioctanoate to methyl stearate was carried out in refluxing methanol for 19 hours using bismuth salts and compounds **4-9** as catalysts (Table 6).

BiCl_3 was the only salt that afforded any appreciable amount of product (26%). Bismuth thiolate compounds **4-6**, **8** and **9** gave very low yields (4-16%). However, compound **7** gave a yield of 75%, outperforming the indium salts and indium thiolates reported previously.²⁶

Conclusion

The reaction of bismuth acetate with polydentate dithiols in 95% ethanol or bismuth nitrate with polydentate (di)thiolates in acetone at room temperature is a facile route to the synthesis of (dithiolato)- and bis(thiolato)bismuth complexes. X-ray crystallography and DFT calculations confirm the preference for a distorted pentagonal pyramidal geometry and the presence of a stereochemically active lone pair in (diamino)(dithiolato)bismuth acetate complexes **4-6**, while both distorted pentagonal pyramidal and distorted trigonal bipyramidal geometries are observed for $(\text{ONS}_2)\text{Bi}(\text{NO}_3)$ (**8**). Although solution NMR shows that solid-state structures are not retained in solution, geminal coupling in $-\text{NCH}_2\text{CH}_2\text{S}-$ groups suggests some restricted motion in the ligand backbones. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and BiCl_3 show high activity toward the esterification of stearic acid, while $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, **4-7** and **9** show very high activity (>90%) toward the transesterification of methyl stearate to butyl stearate. Compound **7** shows moderately high catalytic activity for the transesterification of glyceryl trioctanoate and is more reactive than indium or bismuth salts. Overall, these bismuth compounds show much higher activity than the corresponding indium compounds for esterification/transesterification reactions. We are currently preparing bismuth complexes with other thiolate ligand frameworks and exploring the application of these materials in additional green chemical syntheses.

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Supplementary material

¹H NMR spectra of **4-9**, selected bond distances and angles for **8**, and DFT calculated bond distances and angles for geometry optimized structures. CCDC 1579431-1579436 contains the supplementary crystallographic data for **4-9**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Structures of 1-3

1 **2** **3, E = O, S**

Structural drawings of (di)thiol prolignands.

$\text{H}_2(\text{SNNS})$, $\text{R} = \text{Me}$, $n = 2$
 $\text{H}_2(\text{SNNSPr})$, $\text{R} = \text{Et}$, $n = 3$

$\text{H}_2(\text{NNS}_2)$, $\text{E} = \text{NEt}_2$
 $\text{H}_2(\text{ONS}_2)$, $\text{E} = \text{OMe}$

$\text{H}(\text{NNS})$

Structural drawings of **4-9**.

Figure 1. X-ray crystal structure of **4** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity.

Figure 2. X-ray crystal structure of **5** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity.

Figure 3. X-ray crystal structure of **6** (50% probability ellipsoids). Hydrogen atoms are not shown for clarity.

Figure 4. X-ray crystal structure of **7** (30% probability ellipsoids). Hydrogen atoms are not shown for clarity.

Figure 5. X-ray crystal structure of **8** showing two crystallographically unique molecules (50% probability ellipsoids). Hydrogen atoms are not shown for clarity.

Figure 6. X-ray crystal structure of **9** (30% probability ellipsoids). Hydrogen atoms are not shown for clarity.

Figure 7. Selected DFT-calculated molecular orbitals of [(SNNS)Bi(OAc)] (**4**).

Figure 8. a) ^1H NMR spectrum of **7**, b) Newman projection of the $-\text{SCH}_2\text{CH}_2\text{N}-$ group of **7**.

Figure 9. a) COSY ^1H NMR and b) HSQC NMR spectra of **7**.

Table 1. Crystallographic data for **4-9**.

	4	5	6	7	8	9
formula	C ₁₀ H ₂₁ BiN ₂ O ₂ S ₂	C ₁₃ H ₂₇ BiN ₂ O ₂ S ₂	C ₁₂ H ₂₅ BiN ₂ O ₂ S ₂	C ₉ H ₁₈ BiNO ₃ S ₂	C ₇ H ₁₅ BiN ₂ O ₄ S ₂	C _{17.50} H ₄₁ BiN ₅ O _{3.50} S ²
fw	474.39	516.47	502.44	461.34	464.31	650.65
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
space group	P2 ₁ /c	P2(1)/n	P2(1)/c	P2(1)/n	Pna2(1)	P2(1)/c
<i>a</i> (Å)	13.185(4)	9.964(2)	10.522(2)	9.6609(19)	27.951(6)	11.263(4)
<i>b</i> (Å)	10.796(3)	9.600(2)	11.165(3)	13.082(3)	8.4785(17)	17.635(6)
<i>c</i> (Å)	11.380(3)	18.389(4)	14.238(3)	11.218(2)	22.033(4)	14.288(5)
α (deg)	90	90	90	90	90	90
β (deg)	110.901(3)	102.680(3)	102.636(3)	94.21(3)	90	112.485(4)
γ (deg)	90	90	90	90	90	90
<i>V</i> (Å ³)	1513.3(7)	1716.0(7)	1632.2(7)	1413.9(5)	5221.5(18)	2622.1(15)
<i>Z</i>	4	4	4	4	16	4
<i>F</i> (000)	904	1000	968	872	3488	1296
ρ_{calcd} , g cm ⁻³	2.082	1.999	2.045	2.167	2.363	1.648
μ , mm ⁻¹	11.920	10.521	11.058	12.758	13.827	6.911
<i>T</i> , K	223(1)	173(1)	173(2)	296(1)	173(1)	188(1)
λ , Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>R</i> ₁ ^a	0.0341	0.0297	0.0353	0.0276	0.0406	0.0392
w <i>R</i> ₂ ^b	0.1027	0.0732	0.0926	0.0743	0.0961	0.0979

^a $R_1 = [\sum ||F_o| - |F_c||] / [\sum |F_o|]$ for $[F_o^2 > 2\sigma(F_o^2)]$. ^b $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^4)]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **4-8**.

	4	5	6	7	8		8
Bi1-S1	2.577(2)	2.583(2)	2.613(2)	2.564(2)	2.573(3)	Bi2-S3	2.547(3)
Bi1-S2	2.529(2)	2.525(1)	2.543(2)	2.514(1)	2.528(3)	Bi2-S4	2.547(3)
Bi1-N1	2.564(6)	2.607(4)	2.585(5)	2.568(5)	2.509(10)	Bi2-N3	2.513(11)
Bi1-N2/O3	2.786(5)	2.901(5)	2.919(5)	2.77(4)	2.826(10)	Bi2-O8	2.770(8)
Bi1-O1	2.375(4)	2.393(4)	2.385(4)	2.332(4)	2.498(9)	Bi2-O5	2.514(8)
Bi1-O2	2.874(6)	2.921(6)	2.725(5)	2.709(6)	2.78(1)	Bi2-O6	3.03(1)
S1-Bi1-N1	78.28(13)	77.0(1)	75.5(1)	77.5(1)	77.1(2)	S3-Bi2-N3	79.0(2)
S2-Bi1-N2/O3	73.0(1)	74.7(1)	85.75(9)	86.42(9)	82.7(2)	S4-Bi2-O8	134.4(2)
N1-Bi1-N2/O3	67.8(2)	77.9(1)	67.5(1)	65.1(2)	68.4(3)	N3-Bi2-O8	66.3(3)
S1-Bi1-S2	88.51(6)	99.02(5)	96.02(5)	98.13(5)	99.6(1)	S3-Bi2-S4	101.0(1)
S1-Bi1-O1	83.5(1)	75.7(1)	75.1(1)	79.9(1)	78.2(2)	S3-Bi2-O5	76.7(2)
S2-Bi1-O1	89.3(1)	86.4(1)	91.5(1)	90.9(1)	84.9(2)	S4-Bi2-O5	82.3(2)
S2-Bi1-N1	89.8(1)	89.56(9)	75.5(1)	77.0(1)	77.8(2)	S4-Bi2-N3	79.1(2)
N1-Bi1-O1	161.8(2)	151.4(1)	147.0(1)	152.4(2)	146.9(3)	N3-Bi2-O5	145.8(3)
O1-Bi1-O2	48.8(1)	48.3(1)	50.5(1)	50.7(2)	47.6(4)	O5-Bi2-O6	45.1(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for **9**.

	9
Bi1-S1	2.584(1)
Bi1-S2	2.575(1)
Bi1-N1	2.488(4)
Bi1-N2	2.972(4)
Bi1-N3	2.527(5)
Bi1-N4	3.005(4)
Bi1-O1	3.616(5)
S1-Bi1-S2	93.71(5)
N1-Bi1-N3	152.26(12)
S1-Bi1-N2	143.77(8)
S2-Bi1-N4	141.38(9)
S1-Bi1-N1	77.37(9)
N1-Bi1-N2	66.46(11)
S2-Bi1-N3	75.58(11)
N3-Bi1-N4	65.90(13)
S1-Bi1-O1	96.03(8)
S2-Bi1-O1	143.73(8)

Table 4. Catalyzed conversion of stearic acid to methyl stearate.

Catalyst	Conversion (%)
None	<1
BiCl ₃	100
Bi(NO ₃) ₃ ·5H ₂ O	100
Bi(OAc) ₃	<1
4	<1
5	<1
6	<1
7	<1
8	22
9	<1

Table 5. Catalyzed conversion of methyl stearate to butyl stearate.

Catalyst	Yield (%)
None	4
BiCl ₃	75
Bi(NO ₃) ₃ ·5H ₂ O	98
Bi(OAc) ₃	<1
4	95
5	100
6	97
7	97
8	26
9	90

Table 6. Catalyzed conversion of glyceryl trioctanoate to methyl octanoate.

Catalyst	Conversion (%)
None	<1
BiCl ₃	26
Bi(NO ₃) ₃ ·5H ₂ O	3
Bi(OAc) ₃	<1
4	16
5	7
6	4
7	75
8	6
9	7

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