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Synthesis and Characterization of Gallium and Indium Thiolate Complexes. Crystal and Molecular Structures of $[M(SC_5H_4N)_3]$ (M = Ga, In), $[In(SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$, and $[M_2(OC_2H_4)_2(SC_5H_4N)_4]$ (M = Ga, In)

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The synthesis and characterizations of the monomeric group III thiolate complexes $[In(SC_5H_4N)_3]$ (**1**), $[In(SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**2**), and $[Ga(SC_5H_4N)_3]$ (**5**) and of the binuclear alkoxy-bridged derivatives $[M_2(OC_2H_5)_2(SC_5H_4N)_4]$ (M = In (**3**), Ga (**6**)) are described. Compounds **1** and **2** are formed in the reaction of the appropriate nitrate salt $M(NO_3)_3 \cdot xH_2O$ with the pyridine-2-thiol derivative in ethanol or water in the presence of triethylamine. In contrast, when the reaction is carried out under strictly anaerobic conditions, using the appropriate metal chloride MCl_3 in ethanol solution, the binuclear species **3** and **6** are obtained. Compound **5** was prepared using $GaCl_3$ in THF with pyridine-2-thiol under strictly anaerobic conditions. Compound **4** was prepared under anaerobic conditions in THF solvent from $GaCl_3$ and pyridine-2-thiol. Attempts to prepare complexes of the 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thiol ligand type were unsuccessful. However, the sodium salt $[Na\{SC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2\}]_6 \cdot 2(C_2H_5)_2O$ (**7**) was isolated and the structure characterized. Crystal data: **1**, $C_{15}H_{12}N_3S_3In$, monoclinic, $P2_1$, $a = 8.779(2)$ Å, $b = 11.614(2)$ Å, $c = 9.397(2)$ Å, $\beta = 114.67(3)°$, $V = 870.7(4)$ Å^3, $Z = 2$, 2392 reflections with $I_o > 3\sigma(I_o)$, $R = 0.0338$; **2**, $C_{24}H_{36}N_3S_3Si_3In$, orthorhombic, $Pca2_1$, $a = 11.645(2)$ Å, $b = 19.741(4)$ Å, $c = 14.040(3)$ Å, $V = 3227(2)$ Å^3, $Z = 4$, 1930 reflections, $R = 0.0464$; **3**, $C_{24}H_{26}N_4O_2S_4In_2$, monoclinic, $P2_1/n$, $a = 8.420(2)$ Å, $b = 11.860(2)$ Å, $c = 14.629(3)$ Å, $\beta = 101.83(3)°$, $V = 1429.8(7)$ Å^3, $Z = 2$, 1699 reflections, $R = 0.0296$; **5**, $C_{15}H_{12}N_3S_3Ga$, monoclinic, $P2_1/n$, $a = 8.661(2)$ Å, $b = 11.609(4)$ Å, $c = 9.315(2)$ Å, $\beta = 115.40(3)$ Å, $Z = 2$, 1508 reflections, $R = 0.0453$; **6**, $C_{24}H_{26}N_4O_2S_4Ga_2$, monoclinic, $P2_1/n$, $a = 8.444(2)$ Å, $b = 11.497(2)$ Å, $c = 14.162(3)$ Å, $\beta = 1354.4(7)°$, $Z = 2$, 1513 reflections, $R = 0.0349$; **7**, $C_{124}H_{248}N_6OS_6Si_{12}Na_6$, triclinic, $P\bar{1}$, $a = 16.156(3)$ Å, $c = 17.665(4)$ Å, $\alpha = 118.47(3)°$, $\beta = 92.40(3)°$, $\gamma = 114.75(3)°$, $V = 3757(2)$ Å^3, $Z = 1$, 5125 reflections, $R = 0.0809$.

Introduction

Radioactive congeners of indium (^{111}In, ^{113m}In) and gallium (^{67}Ga, ^{68}Ga) are γ-ray emitters with energies which make them useful for medical imaging.[1] Although the coordination chemistry of thiolate ligands with indium and gallium remains relatively unexplored, the practical potential for the development of materials for medical imaging has been recognized.[2] As previously noted, small neutral complexes will have an improved chance of crossing the blood/brain barrier.[3] A major disadvantage with ^{67}Ga imaging compounds currently in use is the ferric ion metabolic pathway followed by nonspecific compound deposition, resulting in distribution in the liver, blood, and spleen.[4] Thus, body clearance is slow and 72 h may be required to produce images of diagnostic quality.[5] However, the use of the appropriate thiolate ligands should improve the lipophilicity of indium and gallium compounds, thus improving their transport through the body and into target organs for imaging.

Several studies of the biodistribution pattern of indium and/or gallium thiolate compounds have been performed. The cationic indium complex [^{113m}In]TE-BAT has shown promise as a possible myocardial perfusion agent.[6] The neutral [^{67}Ga]-TACN complex is potentially useful for hepatobiliary imaging, but no brain uptake was found.[7] The complexes [^{67}Ga]TACN and [^{67}Ga]MADT have been proposed as myocardial imaging agents.[8]

Moore *et al.*[9] have concluded that coordination of three nitrogens and three sulfurs would provide kinetically stable compounds with potentially useful biodistribution patterns. To increase the lipophilicity of our compounds, we chose pyridine-2-thiol (pys) as a suitable ligand. In the case of the likely tris(pyridine-2-thiolate) complex $[M(pys)_3]$ (M = In, Ga), the materials would exhibit the well-established stability of the tris-chelate complexes and the added potential of facile nucleophilic aromatic substitution chemistry of trisubstituted silyl groups in the 3- and/or 6-positions of pyridine-2-thiol, which should provide a method for modification of biodistribution patterns by appropriate functional group substitution. The class of materials could also be expanded by employing 2-mercaptopyrimidine and its derivatives as the chelating N_3S_3 ligands.

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Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Series 1600 FTIR. All elemental analyses were performed by Oneida Research, Whiteboro, NY 13492. All reactions for gallium and for the ethoxy-bridged compounds were performed under nitrogen using standard Schlenk-line techniques. Ethanol was dried and distilled from magnesium turnings under nitrogen. Tetrahydrofuran (THF) was dried and distilled from the sodium ketyl of benzophenone under nitrogen. All air-sensitive samples were manipulated in a Vac Atmospheres MO 20 drybox under nitrogen.

Preparation of Pyridine-2-thiol. The yellow crystalline solid was prepared by the method of Katritzky.[10] The crude product was rotoevaporated to dryness and Soxhlet-extracted with benzene until no color was evident in the extract. The extract was rotoevaporated to dryness and dissolved in acetone, after which the solution was filtered. The acetone was removed by rotovap, and the resulting solid was stirred with 125 mL of pentane overnight. The mixture was filtered, and the solid was dried under vacuum to give pyridine-2-thiol in 31% yield. IR (KBr pellet, cm^{-1}): 2958 (m), 2876 (m), 1734 (w), 1654 (w), 1571 (vs), 1491 (m), 1438 (m), 1366 (s), 1257 (m), 1180 (m), 1137 (vs), 982 (m), 742 (s), 486 (s).

Preparation of 3-(Trimethylsilyl)pyridine-2-thiol. The yellow crystalline solid was prepared by the method of Block.[11] After sublimation, the crude product (102.4% yield) was washed with acetone and then pentane and crystals were grown by diffusion of pentane into a CH_2Cl_2 solution of the ligand. Recrystallized yield: 40%. IR (KBr pellet, cm^{-1}): 2940 (s), 2854 (s), 1604 (s), 1572 (s), 1309 (vs), 1236 (s), 1203 (m), 1150 (vs), 1122 (s), 1064 (m), 1041 (s), 851 (vs), 749 (vs), 622 (m), 512 (w), 475 (m).

Preparation of 3,6-Bis(*tert*-butyldimethylsilyl)pyridine-2-thiol. The yellow crystalline solid was prepared by the method of Block.[12] The crude product was quenched with H_2O neutralized with HCl. The mixture was rotoevaporated to dryness, dissolved in CH_2Cl_2, and extracted with water. The aqueous layers were extracted with CH_2Cl_2, and the CH_2Cl_2 solutions of the ligand were combined and dried over $MgSO_4$. The solution was filtered, and the filtrate was rotoevaporated to dryness. The desired product was then sublimed from the crude reaction mixture. The sublimed product was washed with hexanes to remove an impurity, to give 6.449 g of pure product (63% yield). IR (KBr pellet, cm^{-1}): 2940 (w), 2849 (w), 1565 (m), 1468 (m), 1289 (s), 1259 (s), 1160 (m), 1141 (s), 1098 (s), 1033 (m), 804 (s), 677 (m), 581 (w), 500 (w).

Preparation of [In(2-C_5H_4NS)$_3$] (1). Method A. In a 50 mL Schlenk flask with a stir bar were placed 0.30 g (0.77 mmol) of $In(NO_3)_3{\cdot}5H_2O$, 0.256 g (2.31 mmol) of pyridine-2-thiol, (C_5H_4NSH), and 10 mL of EtOH. The mixture was stirred for $^1/_2$ h; then 0.30 g (2.97 mmol) of NEt_3 was added dropwise. A white precipitate formed upon addition of the triethylamine. The reaction solution was stirred overnight (this length of time is not required) and then filtered. The precipitate was air-dried to give 0.285 g of $In(C_5H_4NS)_3$ in 84% yield.

Method B. In a 50 mL Schlenk flask with a stir bar were placed 0.10 g (0.256 mmol) of $In(NO_3)_3{\cdot}5H_2O$, 0.085 g (0.769 mmol) of pyridine-2-thiol (C_5H_4NSH), and 10 mL of H_2O. The mixture was stirred for $^1/_2$ h; then 0.08 g (0.769 mmol) of NEt_3 was added dropwise. A white precipitate formed upon addition of the triethylamine. The reaction solution was filtered, and the precipitate was oven-dried to give 0.081 g of $[In(C_5H_4NS)_3]$ in 71% yield. IR (KBr pellet, cm^{-1}): 3000 (m), 1734 (m), 1579 (vs), 1546 (s), 1444 (s), 1416 (vs), 1268 (m), 1136 (vs), 1085 (m), 1038 (m), 1003 (m), 756 (vs), 725 (s), 644 (m), 486 (m), 460 (m). Crystals were grown by diffusion in EtOH into a CH_2Cl_2 solution of $[In(C_5H_4NS)_3]$. Anal. Calcd for $C_{12}H_{12}N_3S_3In$: C, 40.5; H, 2.72; N, 9.44. Found: C, 40.6; H, 2.65; N, 9.48. ^1H NMR (CD_2Cl_2): δ 7.42 (m, 1), 7.56 (m, 1), 7.61 (m, 1), 7.75 (m, 1).

Preparation of [In(2-C_5H_4NS-3-Me_3Si)$_3$] (2). Method A. In a 50 mL Schlenk flask with a stir bar were placed 0.10 g (0.256 mmol) of $In(NO_3)_3{\cdot}5H_2O$, 0.14 g (0.765 mmol) of 3-(trimethylsilyl)pyridine-2-thiol (3-Me_3Si-2-C_5H_4NSH), and 10 mL of EtOH. The mixture was stirred for 1 h; then 0.080 g (7.92×10^{-4} mol) of NEt_3 was added dropwise. A white precipitate formed ca. 10 min after addition of the triethylamine. The reaction solution was stirred for 1 h and then filtered. The precipitate was air-dried to give 0.094 g of [In(3-Me_3Si-2-C_5H_4-NS)$_3$] in 56% yield. IR (KBr pellet, cm^{-1}): 2956 (m), 1570 (s), 1540 (s), 1362 (vs), 1245 (s), 1215 (m), 1138 (m), 1072 (m), 1052 (w), 851 (vs), 760 (s), 694 (w), 673 (m), 626 (w), 487 (vw). Crystals were grown by diffusion of EtOH into a CH_2Cl_2 solution of [In(3-Me_3Si-2-C_5H_4NS)$_3$]. Anal. Calcd for $C_{24}H_{36}N_3S_3Si_3In$: C, 43.6; H, 5.48; N, 6.35. Found: C, 43.0; H, 5.40; N, 6.28. ^1H NMR (CD_2Cl_2): δ 7.76 (dd, 1), 6.96 (dd, 1), 0.39 (s, 9).

Method B. In the drybox, 0.11 g (0.497 mmol) of $InCl_3$ was placed in a 100 mL Schlenk flask with a stir bar. The flask was stoppered and removed from the drybox. Under a flow of nitrogen, 10 mL of dried and distilled EtOH was syringed onto the $InCl_3$. Then, still under nitrogen flow, the Schlenk flask was fitted with a Schlenk addition funnel. Into the Schlenk addition funnel was placed 0.182 g (0.995 mmol) of 3-Me_3Si-2-C_5H_4NSH. The ligand was dried for 10 min under vacuum. To the ligand under a flow of nitrogen was added by syringe 10 mL of dried and distilled EtOH. The ligand solution was added dropwise to the $InCl_3$ solution, and the reaction mixture was stirred for 2 h. To this mixture was added an excess of dried, over CaH_2, NEt_3 in 10 mL of distilled EtOH. A few minutes after the dropwise addition of the base, a precipitate formed. The reaction mixture was stirred for 3 h and then filtered under a flow of nitrogen. The product was dried under vacuum to give 0.034 g of [In(3-Me_3Si-2-C_5H_4NS)$_3$]. Crystals were grown by diffusion of EtOH into a CH_2Cl_2 solution of [In(3-Me_3Si-2-C_5H_4NS)$_3$].

Method C. In a 50 mL Schlenk flask with a stir bar were placed 0.10 g (2.56×10^{-4} mol) of $In(NO_3)_3{\cdot}5H_2O$, 0.140 g (7.69×10^{-3} mol) of 3-(trimethylsilyl)pyridine-2-thiol (3-Me_3Si-2-C_5H_3NSH), and 10 mL of H_2O. The mixture was stirred for $^1/_2$ h; then 0.08 g (7.69×10^{-4} mol) of NEt_3 added dropwise. The ligand did not totally dissolve in H_2O, and the extent of reaction was limited by the solubility of the ligand. By IR analysis, i.e. comparison of the peak heights for product and starting material, the yield was approximately 10%.

Preparation of $[In_2(OEt)_2(2\text{-}C_5H_4NS)_4]$ (3). In the drybox, 0.15 g (0.678 mmol) of $InCl_3$ was placed a 100 mL Schlenk flask with a stir bar. The flask was stoppered and removed from the drybox. Under a flow of nitrogen, 10 mL of dried and distilled EtOH was syringed onto the $InCl_3$. Then, still under nitrogen flow, the Schlenk flask was fitted with a Schlenk addition funnel. Into the Schlenk addition funnel was placed 0.15 g (1.36 mmol) of 2-C_5H_4NSH. The ligand was dried for 10 min under vacuum. Onto the ligand under a flow of nitrogen was syringed 5 mL of dried and distilled EtOH. The ligand solution was added dropwise to the In(III)−ethoxide solution. The Schlenk addition funnel was rinsed with 5 mL of distilled EtOH. The reaction mixture was stirred overnight. To this mixture was added an excess of NEt_3, dried over CaH_2, in 10 mL of distilled EtOH. A few minutes after the dropwise addition of the base, a precipitate formed. The reaction mixture was stirred for 7 h and then filtered under a flow of nitrogen. The product was dried under vacuum to give 0.08 g of $[In_2(OEt)_2(2\text{-}C_5H_4NS)_4]$ in 31% yield. IR (KBr pellet, cm^{-1}): 2996 (w), 2857 (w), 1581 (vs), 1544 (s), 1438 (s), 1420 (vs), 1263 (m), 1134 (s), 1085 (m), 1050 (s), 1005 (m), 884 (m), 760 (s), 750 (s), 726 (s), 644 (m), 480 (s). Crystals were grown by diffusion of EtOH into a CH_2Cl_2 solution of $[In_2(OEt)_2(2\text{-}C_5H_4NS)_4]$. Anal. Calcd for $C_{24}H_{36}N_4O_4S_4In_2$: C, 37.9; H, 3.45; N, 7.37. Found: C, 37.7; H, 3.77; N, 7.38.

Preparation of [In(pyr)$_3$] (4). In a 50 mL Schlenk flask with a stir bar were placed 0.10 g (0.256 mmol) of $In(NO_3)_3{\cdot}5H_2O$, 0.086 g (0.767 mmol) of 2-pyrimidinethiol, and 10 mL of EtOH. The mixture was stirred for 1 h; then 0.080 g (0.792 mmol) of NEt_3 was added dropwise. The yellow color disappeared within 30 s of the addition of the triethylamine. The reaction solution was stirred for 1 h to allow the tan particles to go into solution. The reaction solution was filtered, and the product was dried under vacuum. Crystals were grown by diffusion of EtOH into a CH_2Cl_2 solution of $[In(C_4H_3N_2S)_3]$ to give 0.017 g of [In(pyr)$_3$] in 14.7% yield. IR (KBr pellet, cm^{-1}): 3102 (w), 3057 (w), 2962 (w), 1570 (s), 1540 (s), 1427 (m), 1379 (vs), 1248 (m), 1215 (w), 1184 (m), 1082 (w), 801 (m), 764 (m), 746 (m), 650 (m). ^1H NMR (CD_2Cl_2): δ 8.57 (d, 2), 7.12 (t, 1).

Preparation of [Ga(2-C_5H_4NS)$_3$] (5). In the drybox, 0.27 g (1.53 mmol) of $GaCl_3$ was placed in a 100 mL Schlenk flask with a stir bar.

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Table 1. Crystallographic Data for the Structural Studies of $[In(SC_5H_4N)_3]$ (**1**), $[In(SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**2**), $[In(OC_2H_5)_2(SC_5H_4N)_4]$ (**3**), $[Ga(SC_5H34N)_3]$ (**5**), $[Ga_2(OC_2H_5)_2(SC_5H_4N)_4]$ (**6**), and $[Na\{SC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2\}]_6{\cdot}2(C_2H_5)_2O$ (**7**)

	1	**2**	**3**	**5**	**6**	**7**
chem formula	$C_{15}H_{12}N_3S_3In$	$C_{24}H_{36}N_3S_3Si_3In$	$C_{24}H_{26}N_4S_4O_2In_2$	$C_{15}H_{12}N_3S_3Ga$	$C_{24}H_{26}N_4O_2S_4Ga_2$	$C_{124}H_{248}N_6OS_6Si_{12}Na_6$
a, Å	8.779(2)	11.645(2)	8.420(2)	8.661(2)	8.444(2)	16.156(3)
b, Å	11.614(2)	19.741(4)	11.860(2)	11.609(4)	11.497(2)	17.299(3)
c, Å	9.397(2)	14.040(3)	14.629(3)	9.315(2)	14.162(3)	17.665(4)
α, deg						118.47(3)
β, deg	114.67(3)		101.83(3)	115.40(3)	99.89(3)	92.40(3)
γ, deg						114.75(3)
V, Å^3	870.7(4)	3227(2)	1429.8(7)	846.0(4)	1354.4(7)	3757(2)
Z	2	4	2	2	2	1
fw	445.3	661.8	760.4	400.2	670.2	2254.2
space group	$P2_1$	$Pca2_1$	$P2_1/n$	$P2_1$	$P2_1/n$	$P\bar{1}$
T, °C	−60	−60	−60	−60	−60	−60
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
D_{calc}, g cm^{-3}	1.698	1.362	1.766	1.571	1.106	0.996
μ, cm^{-1}	17.15	10.55	19.34	19.94	23.28	2.42
R	0.0338	0.0464	0.0296	0.0453	0.0349	0.0809
R_w	0.0442	0.0575	0.0580	0.0483	0.0511	0.1006

$^a\ \sum|F_o| - |F_c||/\sum|F_o|$. $^b\ [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Comparison of Selected Bond Lengths (Å) and Angles (deg) for the Structures of $[In(SC_5H_4N)_3]$ (**1**), $[In(SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**2**), and $[Ga(SC_5H_4N)_3]$ (**5**)

	1	**2**	**5**
M−S	2.520(2)	2.541(3)	2.426(2)
	2.543(2)	2.535(3)	2.409(3)
	2.530(1)	2.542(3)	2.426(3)
M−N	2.315(5)	2.338(9)	2.077(8)
	2.310(5)	2.303(10)	2.046(8)
	2.328(6)	2.299(9)	2.091(6)
S−C	1.761(8)	1.764(12)	1.712(10)
	1.743(7)	1.764(14)	1.737(10)
	1.733(6)	1.760(12)	1.716(11)
S···N	2.618(6)	2.600(10)	2.564(10)
	2.605(6)	2.590(11)	2.573(10)
	2.609(6)	2.586(11)	2.575(10)
S1−M−S2	107.0(1)	107.8(1)	102.8(1)
S1−M−S3	112.3(1)	112.8(1)	105.0(1)
S2−M−S3	109.0(1)	104.4(1)	100.1(1)
S1−M−N1	65.4(1)	64.2(2)	68.9(2)
S2−M−N1	99.0(2)	102.7(2)	160.6(2)
S3−M−N1	150.7(2)	152.0(2)	99.0(2)
S1−M−N2	151.6(2)	145.2(2)	97.1(2)
S2−M−N2	64.7(2)	64.5(3)	69.9(3)
S3−M−N2	95.9(2)	101.9(2)	157.3(2)
S1−M−N3	101.0(1)	103.3(2)	159.1(3)
S2−M−N3	151.2(1)	148.8(2)	98.0(3)
S3−M−N3	64.8(1)	64.4(2)	69.0(2)
N1−M−N2	88.3(2)	83.8(3)	93.3(3)
N1−M−N3	86.6(2)	88.7(3)	91.8(3)
N2−M−N3	87.4(2)	88.4(3)	91.7(3)

The flask was stoppered and removed from the drybox. Under nitrogen flow, the Schlenk flask was fitted with a Schlenk addition funnel. Into the Schlenk addition funnel was placed 0.68 g (6.14 mmol) of $2\text{-}C_5H_4NSH$. The ligand was dried for 10 min under vacuum. Onto the ligand under a flow of nitrogen was syringed 50 mL of dried and distilled THF. The ligand solution was added dropwise to the $GaCl_3$, and the reaction mixture was stirred overnight. To the reaction mixture was added an excess of dried, over CaH_2, NEt_3 in 10 mL of distilled THF. A few minutes after the dropwise addition of the base, a precipitate formed. The reaction mixture was stirred for 3$^1/_2$ h and then filtered under a flow of nitrogen. The product was dried under vacuum to give 0.59 g of $[Ga(2\text{-}C_5H_4NS)_3]$ in 97% yield. IR (KBr pellet, cm^{-1}): 2964 (m), 1582 (s), 1444 (s), 1420 (s), 1262 (vs), 1136 (vs), 1084 (vs), 1032 (vs), 801 (vs), 755 (s), 729 (m), 647 (w), 487 (m). Crystals were grown by diffusion of hexane into a CH_2Cl_2 solution of $[Ga(C_5H_4NS)_3]$. Anal. Calcd for $C_{15}H_{12}N_3S_3Ga$: C, 45.02; H, 3.02; N, 10.50. Found: C, 43.34; H, 3.17; N, 10.07.

Preparation of $[Ga_2(OEt)_2(2\text{-}C_5H_4NS)_4]$ (6). Method A. In the drybox, 0.11 g (0.625 mmol) of $GaCl_3$ was placed a 100 mL Schlenk flask with a stir bar. The flask was stoppered and removed from the drybox. Under a flow of nitrogen, the Schlenk flask was fitted with a Schlenk addition funnel. Into the Schlenk addition funnel was placed 2−6 equiv of $2\text{-}C_5H_4NSH$ (the amount does not matter as long as 2 equiv is present). The ligand was dried for 10 min under vacuum. Onto the ligand under a flow of nitrogen was syringed 10 mL of dried and distilled EtOH. The ligand solution was added dropwise to the $GaCl_3$. The Schlenk addition funnel was rinsed with 10 mL of distilled EtOH, and the reaction mixture was stirred overnight. To the reaction mixture was added an excess of dried, over CaH_2, NEt_3 in 10 mL of distilled EtOH. A few minutes after the dropwise addition of the base, a precipitate formed. The reaction mixture was stirred for 2 h and then filtered under a flow of nitrogen. The product was dried under vacuum to give 0.07 g of $[Ga_2(OEt)_2(2\text{-}C_5H_4NS)_4]$ in 34% yield. IR (KBr pellet, cm^{-1}): 2961 (m), 1734 (m), 1583 (s), 1546 (s), 1438 (s), 1420 (s), 1262 (s), 1136 (s), 1086 (m), 1053 (s), 1013 (m), 896 (m), 760 (m), 750 (s), 731 (m), 650 (m), 523 (m), 477 (m). Crystals were grown by diffusion of EtOH into a CH_2Cl_2 solution of $[Ga_2(OEt)_2(2\text{-}C_5H_4NS)_4]$. Anal. Calcd for $C_{24}H_{26}N_4O_2S_4Ga_2$: C, 43.0; H, 3.91; N, 8.36. Found: C, 42.4; H, 3.80; N, 8.31.

Method B. Crystals of $[Ga_2(OEt)_2(2\text{-}C_5H_4NS)_4]$ were grown by diffusion of EtOH into a CH_2Cl_2 solution of $[Ga(C_5H_4NS)_3]$.

Preparation of Na[3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thiolate] (7). In a 100 mL Schlenk flask was placed 0.520 g (1.53 mmol) of 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thiol. The compound was dried briefly under vacuum. To the ligand was added 20 mL of THF under a flow of nitrogen, and to this solution was added a slight excess of sodium spheres. The reaction mixture was stirred overnight under nitrogen until the evolution of hydrogen ceased. The Schlenk flask was then fitted with a condenser under a flow of nitrogen, and the reaction mixture was refluxed for 2 days. The reaction mixture became orange after refluxing. The excess sodium was removed by filtration under nitrogen, and the product was dried under vacuum to give a quantitative yield of the product. IR (KBr pellet, cm^{-1}): 2954 (m), 2857 (m), 1564 (m), 1468 (m), 1363 (w), 1290 (m), 1262 (m), 1163 (m), 1141 (s), 1101 (s), 1033 (s), 805 (s), 679 (m). Crystals of Na[3,6-bis(*tert*-butyldimethylsilyl)pyridinethiolate] were grown by slowly cooling a saturated hexane solution.

X-ray Crystallography. Compounds **1**−**3** and **5**−**7** were studied using a Rigaku AFC5S diffractometer, equipped with a low-temperature device. Since the crystals degraded slowly at room temperature, data collection was carried out at 213 K. Crystal stability was monitored using five medium-intensity reflections in each case, and no significant changes in the intensities of the standards were observed over the course of the data collections. The crystal parameters and other experimental details of the data collections are summarized in Table 1. A complete description of the details of the crystallographic methods is given in the supporting information, as well as the atomic positional parameters.

The structures were solved by the Patterson method and refined by full-matrix least squares. The details of the structure solutions and refinements are presented in the supporting information. No anomalies were encountered in the refinements of the structures. Bond lengths and angles for the structures of **1**−**3** and **5**−**7** are listed in Tables 2−5.

Table 3. Comparison of Selected Bond Lengths (Å) and Angles (deg) for the Structures of $[In_2(OC_2H_5)_2(SC_6H_4N)_4]$ (**3**) and $[Ga(OC_2H_5)_2(SC_6H_4N)_4]$ (**6**)

	3	6
M−S	2.552(1)	2.433(1)
	2.545(1)	2.428(1)
M−O	2.142(3)	1.955(3)
	2.122(3)	1.944(3)
M−N	2.301(4)	2.113(4)
	2.291(4)	2.100(4)
S−C	1.757(5)	1.733(5)
	1.745(5)	1.732(4)
S···N	2.611	2.586(4)
	2.608	2.583(4)
S1−M−S2	100.3(1)	95.4(1)
S1−M−O1	154.4(1)	163.3(1)
S2−M−O1	104.9(1)	101.2(1)
S1−M−N1	64.9(1)	68.9(1)
S2−M−N1	151.2(1)	155.1(1)
O1−M−N1	90.4(1)	94.9(1)
S1−M−N2	94.2(1)	91.0(1)
S2−M−N2	65.0(1)	69.1(1)
O1−M−N2	92.4(1)	93.8(1)
N1−M−N2	90.5(1)	91.2(1)
S1−M−O1a	104.1(1)	101.3(1)
S2−M−O1a	104.0(1)	101.2(1)
O1−M−O1a	74.3(1)	76.8(1)
N1−M−O1a	103.7(1)	100.9(1)
N2−M−O1a	160.3(1)	165.2(1)

Results and Discussion

The tris-chelate complexes of indium $[In(2\text{-}C_5H_4NS)_3]$ (**1**), $[In(2\text{-}C_5H_4NS\text{-}3\text{-}Me_3Si)_3]$ (**2**), and [In(pyr)$_3$] (**4**) were synthesized by relatively straightforward means in ethanol or water as reaction solvent. Compound **1** was isolated in good yield from the reaction of $In(NO_3)_3\cdot5H_2O$, pyridine-2-thiol, and NEt_3 in the mole ratio 1:3:3 in either EtOH or H_2O as solvent. Compound **2** was synthesized by analogous means, employing either $In(NO_3)_3\cdot5H_2O$ or $InCl_3$ as the indium precursor. In contrast, the pyrimidine-2-thiol analogue **4** could be isolated in good yield only from the reaction of $In(NO_3)_3\cdot5H_2O$ with pyrimidine-2-thiol and NEt_3 in EtOH.

However, the synthesis of the Ga(III) complex $[Ga(2\text{-}C_5H_4NS)_3]$ (**5**) could be effected only from $GaCl_3$ under rigorously anhydrous conditions. Attempts to prepare **5** from $Ga(NO_3)_3\cdot xH_2O$ produced gallium hydroxide only. Furthermore, attempts to recrystallize **5** from diffusion of H_2O into THF solutions resulted in the isolation of pyridine-2-thiol.

The ethoxy-bridged compounds $[In_2(OEt)_2(2\text{-}C_5H_4NS)_4]$ (**3**) and $[Ga_2(OEt)_2(2\text{-}C_5H_4NS)_4]$ (**6**) were produced by first reacting MCl_3 (M = Ga, In) with dried EtOH, followed by addition of the alkoxide mixture (which was not characterized) to ligand and base. The binuclear alkoxy-bridged compounds, **3** and **6**, appear to have considerable stability. Attempted reaction of $[In_2(OEt)_2(2\text{-}C_5H_4NS)_3]$ with $3\text{-}Me_3Si\text{-}2\text{-}C_5H_4NSH$ did not incorporate the silylated ligand. This behavior is unusual in that $[In(3\text{-}Me_3Si\text{-}2\text{-}C_5H_4NS)_3]$ was produced under all reaction conditions with indium and the $3\text{-}Me_3Si\text{-}2\text{-}C_5H_4NSH$ ligand. Reaction of $In(NO_3)_3$ with 2 equiv of $2\text{-}C_5H_4NSH$ in EtOH with base produces an insoluble white solid, suggesting that a polymeric material was formed.

It is unusual that $[In(2\text{-}C_5H_5NS\text{-}3\text{-}SiMe_3)_3]$ (**2**) was always isolated even in attempts to prepare the ethoxy-bridged binuclear analogues to **3** using with limited amounts of ligand, while gallium did not react with the trimethylsilyl-derivatized ligand to produce a characterizable compound under any conditions. Neither indium(III) or gallium(III) chlorides appeared to react with the 3,6-bis(*tert*-butyldimethylsilyl)pridine-2-thiol. In a typical reaction, the sodium salt of 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thiolate was prepared by reaction of the ligand with sodium in THF. Stirring the sodium salt with $InCl_3$ or $GaCl_3$ followed by crystallization yielded only the "wagon wheel" structure of Na[3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thiolate] (**7**), which is analogous to the structures of the silver(I) and copper(I) salts of pyridine-2-thiol.[13]

The lipophilicity of these compounds is demonstrated by their solubility in such organic solvents as THF and CH_2Cl_2. The indium compounds are indefinitely stable in H_2O/DMF solution. However, the insolubility of the indium compounds in H_2O indicates that to study the biodistribution of these compounds would require a medium which contains less polar environments, such as blood plasma, or introduction in mixed solvents, such as H_2O/DMF. The gallium compounds, in contrast, could only be prepared under anhydrous conditions, which greatly limits their potential applications to medical imaging.

The ^1H NMR spectra of the water-stable indium compounds are relatively unexceptional and appear first order for **1** and **4** while that of compound **2** appears to be second order. The

Table 4. Summary of Structural Parameters for Gallium and Indium Thiolate Complexes[24,25]

compound	coordn no. M	coordn no. S	M−S, Å	M−N, Å	M−X(X), Å	S−C, Å	M−S−C, deg	ref
$[Ga(SC_6H_2\text{-}2,4,6\text{-}Bu^t_3)_3]$	2	2	2.205(6)			1.807	100.4	18
$[Bu^nGa_2(SC_6H2\text{-}2,4,6\text{-}Bu^t_3)_2]$	3	2	2.21(1)					18
$[Ph_2Ga(SEt)]_2$	4	3	2.379(3)		2.083	1.838	104.3(6)	24b
$[Pr^n_4N][Ga(SEt)_4]$	4	2	2.264(3)			1.75(1)	103.6(6)	17
$[Et_4N]_2[Ga_2S_2(SPh)_4]$	4	2	2.284		2.269(1)(S)	1.762(4)	108.1(2)	17
$[Ga_4I_4S_2(SMe)_4]$	4	3	2.336(7)		2.204(8)(S) 2.516(3)(I)			15
$[Ga_2I_4(SMe)_2]$	4	3	2.379(5)		2.495(3)(I)	1.87(2)		16
$[GaCl(S_2N_2)]$	5	2	2.252(2)	2.144(3)	2.365(1)(Cl)			19
$[Ga(SC_5H_4N)_3]$	6	2	2.420(3)	2.071(9)		1.722(12)	78.2(5)	this work
$[Ga_2(OC_2H_5)_2(SC_5H_4N)_4]$	6	2	2.431(2)	2.107(4)		1.733(6)	78.3(2)	this work
$[Mes_2In(SBu^t)]_2$[a]	4	2	2.619(5)		2.107(8)	*b*	*b*	25
$[Mes_2In(S\text{-}amyl^t)]_2$	4	2	2.592(4)		2.22(1)	*b*	*b*	25
$[Mes_2In(SSiPh_3)]_2$	4	2	2.621(1)		2.176(4)	*b*	*b*	25
$[Mes_2In(SSiPh_3)]_3$	4	2	2.617(6)		2.12(1)	*b*	*b*	25
$[In(SC_5H_2\text{-}2,4,6\text{-}Bu^t)_3]$	3	2	2.398(4)			1.808(11)	98.1(3)	24b
$[In(SC_6H_2\text{-}2,4,6\text{-}CF_3)_3(OEt_2)]$	4	2	2.418(3)		2.244(6)(O)	1.786(8)	104.1(3)	24c
$[Ph_4P][BrIn(SPh)_3]$	4	2	2.450(4)		2.527(I)	1.75(3)	107.7(7)	24d
$[In(SC_5H_4N)_3]$	6	2	2.531(2)	2.318(6)		1.746(8)	81.5(3)	this work
$[In(SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$	6	2	2.539(3)	2.313(10)		1.763(14)	82.5(4)	this work
$[In_2(OC_2H_5)_2(SC_5H_4N)_4]$	6	2	2.549(1)	2.296(4)	2.132(3)(O)	1.733(4)	80.9(2)	this work

[a] Mes = 2,4,6-trimethylphenyl. [b] Not reported.

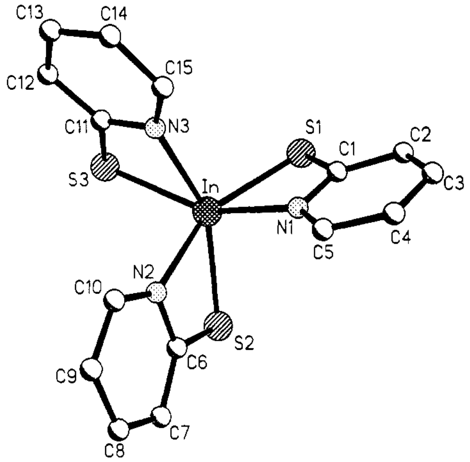

Figure 1. View of the structure of $[In(SC_5H_4N)_3]$ (**1**), showing the atom-labeling scheme.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for the Structure of $[Na\{SC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2\}]_6 \cdot 2(C_2H_5)_2O$ (**7**)

Na1−S1	2.853(4)	S1−C	1.759(9)
Na1−S2	2.803(5)	S2−C	1.771(6)
Na1−S3	2.857(5)	S3−C	1.756(9)
Na7−S1	2.819(4)	S···N	2.653(7)
Na2−S2	2.785(4)		2.663(8)
Na2−S3	2.811(5)		2.664(8)
Na3−S1	2.812(3)	S1−Na1−S2	100.5(1)
Na3−S2	2.790(5)	S1−Na1−S3	94.1(1)
Na3−S3	2.831(5)	S2−Na1−S3	101.5(1)
Na1−N1	2.518(8)	S1−Na1−N1	138.7(3)
Na2−N2	2.461(7)	S2−Na1−N1	59.8(2)
Na3−N3	2.465(9)	S3−Na1−N1	123.3(2)
S1−Na2−S3a	103.3(1)	S1A−Na3−S3	103.0(1)
S2−Na2−S3a	95.8(1)	S2−Na3−S3	102.5(1)
S2−Na2−S3a	101.6(1)	S1A−Na3−N3	121.6(2)
S1−Na2−N2	59.9(2)	S2−Na3−N3	125.5(2)
S2−Na2−N2	136.1(2)	S3−Na−N3	59.9(2)
S3A−Na2−N2	126.0(2)		

integration is in accord with the crystal structure and elemental analysis data.

Description of the Structures. As shown in Figure 1, the structure of $[In(SC_5H_4N)_3]$ (**1**) consists of discrete monomeric, neutral molecules. The indium atom is coordinated in a distorted octahedral array by three thiolate donors and three pyridyl nitrogen donors in the *facial* orientation. The average In−S distance is 2.531(5) Å and falls in the narrow range 2.520(2)−2.543(3) Å, while the average In−N distance is 2.318(7) Å with a range of 2.310(5)−2.328(6) Å. The aromatic rings of the $(SC_5H_4N)^-$ ligands form a propeller-like arrangement around the S_3 plane. The valence angles at the In center are considerably distorted from the idealized octahedral limits as a consequence of chelate ring formation, a characteristic most apparent in the internal chelate angles, S−In−N, of 65.4(1), 64.7(2), and 64.8(1)°. The average chelate "bite" distance S- - -N is 2.61 Å.

The structures of $[In(SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**2**) and $[Ga(SC_5H_4N)_3]$ (**5**) are analogous to that of **1**, exhibiting the same *fac* orientation of the ligands and unexceptional metrical parameters, as shown in Table 2. Comparison of the structural data for **1** and **2** reveals that the introduction of the trimethylsilyl substituent in the 3-position of the ring has a negligible influence on the structural features associated with the $[InS_3N_3]$ core. In the case of the gallium compound **5**, the only pronounced structural differences are associated with the shorter Ga−S and Ga−N bond distances, consequent to the smaller covalent radius of gallium relative to indium. Internal ligand parameters for **1**, **2**, and **5** are similar to those previously reported for pyridine-2-thiol and 3-(trimethylsilyl)pyridine-2-thiol acting as bidentate ligands through S and N donor atoms.[14] While compounds **1**, **2**, and **5** exhibit the *fac* coordination mode both in the solid state and in solution, it is curious that the analogous tris-chelate complexes $[M(SC_5H_4N)_3]$ and $[M(SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ of Co(III) and Rh(III) display the meridional arrangement of ligands.[14t,u]

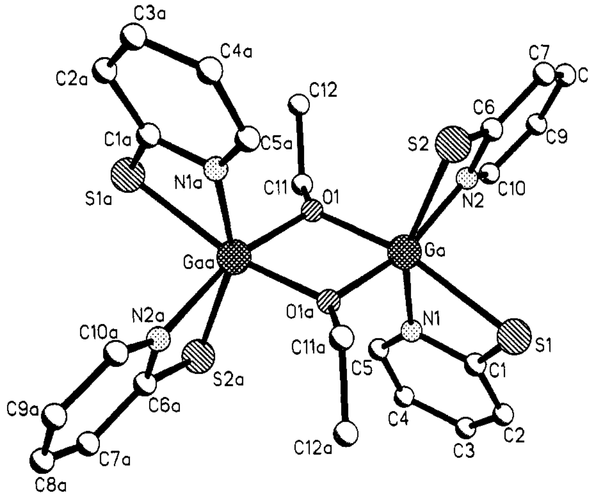

Figure 2. Structure of $[Ga_2(OC_2H_5)_2(SC_5H_4N)_4]$ (**5**), showing the atom-labeling scheme.

The structural core of the binuclear complexes $[In_2(OC_2H_5)_2(SC_5H_4N)_4]$ (**3**) and $[Ga_2(OC_2H_5)_2(SC_5H_4N)_4]$ (**6**) is illustrated in Figure 2. The structures consists of discrete binuclear, neutral molecules with the metal centers in distorted octahedral geometries. Taking structure **3** as the prototype, each indium site is coordinated to two pyridine-2-thiol ligands in the usual chelate coordination geometry and to two bridging alkoxide oxygen donors to produce the $[InS_2N_2O_2]$ core. The central $[In_2O_2]$ rhombus exhibits symmetrically bridging OR groups with an average In−O distance of 2.132(5) Å. The pyridine-2-thiolate ligands are so disposed as to position the thiolate sulfur of one ligand and the pyridyl nitrogen of the second approximately in the plane of the $[In_2O_2]$ rhombus and hence in a transoid orientation relative to the oxygen donors. The

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Table 6. Comparison of Structural Features for Hexanuclear Metal Thiolates of the Class $[M\{SC_6H_{4-n}N(SiR_3)_n\}]$ (M = Na, Cu, Ag)

	coordn no.					
	M	S	M−S, Å	M−N, Å	M−M, Å	ref
$[Na\{SC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2\}]_6$	4	3	2 × 2.831(5) 1 × 2.792(5)	2.481(9)	6 × 3.489(4) all others greater than 4.77 Å	this work
$[Cu(SC_5H_3N\text{-}3\text{-}SiMe_3)]_6$	3	3	2 × 2.245(2)	2.030(5)	6 × 2.832(1) 6 × 3.144(1)	22
$[Cu(SC_5H_4N)]_6$	3	3	2 × 2.241(3)	2.034	6 × 2.826(1) 6 × 3.073(1)	20
$[Ag(SC_5H_3N\text{-}3\text{-}SiMe_3)]_6$	3	3	2 × 2480(3)	2.317(12)	6 × 3.016(2) 6 × 3.157(2)	21

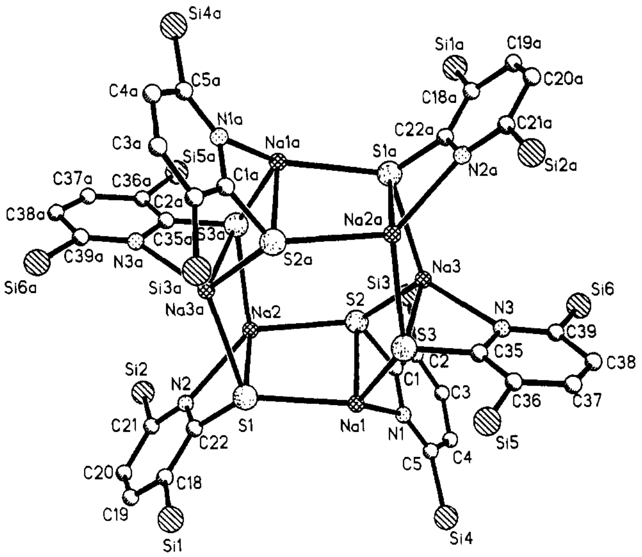

Figure 3. Perspective view of the structure of $[Na(SC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2]_6$ (**7**). The methyl and butyl groups have been omitted for clarity.

structural parameters associated with the pyridine-2-thiolate groups are unexceptional.

Thiolate derivatives of Ga and In remain relatively unexplored, and only a few such complexes have been structurally characterized. Furthermore, compounds **1**−**6** represent the first examples of thiolate complexes of Ga and In possessing six-coordinate cores. Table 4 summarizes the structural information available for thiolate complexes of Ga and In. For both Ga and In, there is a clearly defined dependence of the M−S distance on the coordination number of the metal and the sulfur. As anticipated, increasing the metal coordination number increases steric interactions and results in lengthening of the M−S distances. Likewise, M−S distances for bridging thiolate ligands are expanded relative to those for terminally coordinated sulfur. Thus, Ga−S distances in the range 2.36−2.40 Å were observed for the thiolate-bridged complexes $[Ga_4I_4S_2(SCH_3)_4]$,[15] $[Ga_2I_4(SCH_3)_2]$, and $[Ph_2Ga(SEt)]_2$,[16] while the similarly four-coordinate mononuclear species $[(n\text{-}Pr)_4N][Ga(SEt)_4]$ and $[Et_4N]_2[Ga_2S_2(SPh)_4]$[17] exhibit distances of 2.257(9) and 2.264(3) Å, respectively.

On the other hand, Ga−S distances for three-coordinate complexes $[Ga(SC_6H_2\text{-}2,4,6\text{-}Bu^t_3)_3]$ and $[(n\text{-}Bu)Ga(SC_6H_2\text{-}2,4,6\text{-}Bu^t_3)_2]$[18] are only marginally shorter than those for the four-coordinate mononuclear species cited above and for the five-coordinate $[GaCl(S_2N_2)]$.[19] However, the six-coordinate species of this study, **3** and **6**, exhibit significantly longer Ga−S bond distances than the other examples of Ga−thiolate complexes reported in the table. This pronounced elongation may reflect, in part, the consequences of chelate ring formation, as well as simple steric crowding associated with the increased coordination number. The formation of the four-membered Ga−S−C−N ring imposes steric constraints most notably observable in the S−Ga−N valence angles, which are considerably distorted from the octahedral ideal of 90°. Consequently, the overlap of metal and ligand orbitals is not maximal, and some lengthening of the distances is anticipated.

The consequences of chelate ring formation are also apparent in the Ga−S−C angles of **3** and **6** which are contracted to *ca.* 78° compared to values of 100−108° in monodentate thiolate ligands. This effect also appears to correlate with the contraction of the S−C bond length in the chelate complexes, an observation which suggests some delocalization of multiple-bond character throughout the ring.

The indium−thiolate complexes listed in Table 4 exhibit structural trends similar to those discussed for the gallium analogues. The large difference in the Ga−S and In−S distances is primarily a result of the small relative size and lower electropositive character of gallium owing to the filling of the 3d shell.

Attempts to isolate Ga(III) and In(III) complexes of the 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thiol ligand resulted in the isolation of the sodium salt of the ligand $[Na\{SC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)\}]_6{\cdot}2(C_2H_5)_2O$ (**7**). As shown in Figure 3, the structure of **7** may be described as a paddlewheel, with the central cylinder constructed from two Na_3S_3 heterocyclic rings and with the $-C_5H_2N(SiMe_2Bu^t)_2$ ligand fragments providing the six paddles. The structure is grossly similar to those previously reported for $[Cu(SC_5H_4N)_3]$,[20] $[Cu(SC_5H_3NSiMe_3)_6]$,[21] and $[Ag(SC_5H_3NSiMe_3)_6]$.[22] However, the sodium analogue **7** exhibits significant differences in detail from the structures of the Cu(I) and Ag(I) derivatives. As summarized in Table 6, the latter clusters exhibit distorted trigonal-planar geometries about the $\{MS_2N\}$ metal sites. In contrast, the geometry about the Na sites of **7** is highly distorted four-coordinate (NaS_3N). Furthermore, the M_6 cores of the Cu(I) and Ag(I) derivatives are distorted octahedra with two mutually *trans* faces exhibiting slightly expanded M−M distances with respect to the remaining six M−M distances. The sodium cluster exhibits only six Na−Na close contacts in the range 3.454(2)−3.531(2) Å, with no other Na−Na distances shorter than 4.77 Å. As shown in Figure 4, this pattern of Na−Na contacts produces a hexanuclear ring with the chair configuration and consequently a structure of less regular dimensions.

The thiolate sulfur donors of the Cu(I) and Ag(I) derivatives each bridge two metal sites, while those of **7** are triply-bridging

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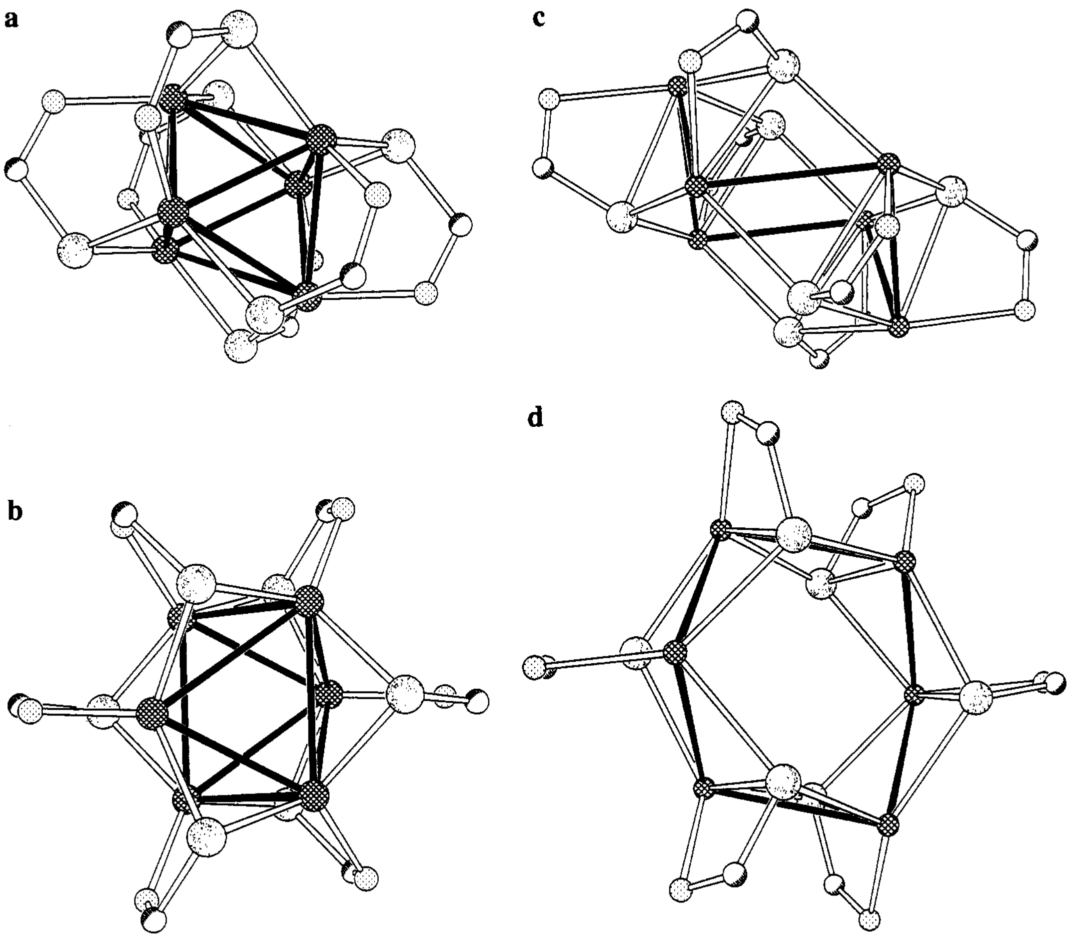

Figure 4. (a, b) Two views of the $[M_6(SCN)_6]$ core of $[Cu\{SC_5H_3N\text{-}3\text{-}SiMe_3\}]_6$. (c, d) Corresponding views of the $[Na_6(SCN)_6]$ core of **7**.

with Na−S bond distances in the narrow range 2.785(4)−2.853(4) Å. Thus, while the Cu(I) and Ag(I) structures exhibit exclusively M_3S_3 rings, the sodium structure **7** possesses Na_2S_2 rhombi in addition to the two Na_3S_3 faces.

To our knowledge, there is only one other example of a structurally characterized sodium−thiolate species, the polymeric $[Na\{SC_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}(thf)_2]$.[23] The average Na−S distance of 2.833(4) Å in the latter may be compared to that of 2.818(6) Å observed for **7**. The Na−S bond distances suggest relatively weak coordination of sulfur donors to Na^+. The irregular geometry about the Na sites in **7** may be attributed to the ionic nature of the Na−S and Na−N interactions. The low degree of orbital overlaps presumably results in less stringent directional requirements for the bonds. In the case of $[Na(SC_6H_2\text{-}2,4,6\text{-}(CF_3)_3)(thf)_2]$, the oxophilic sodium bonds to two oxygen donors from thf molecules at *ca.* 2.27 Å. It is a curious feature of **7** that, even in the presence of ether donors, the Na^+ site retains the $\{NaS_3N\}$ coordination core.

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Supporting Information Available: Tables giving details of data collection and refinement, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and calculated hydrogen atom positions for **1**−**3** and **5**−**7** (52 pages). Ordering information is given on any current masthead page.

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