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Article

New Metalloligands $[M(SC\{O\}Ph)_4]^-$: Synthesis and Characterization of Polymeric $[A(MeCN)_x\{M(SC\{O\}Ph)_4\}]$ Compounds (A = Li, Na and K; M = Ga and In; x = 0–2)

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Exploiting the ability of the $[M(SC\{O\}Ph)_4]^-$ anion to behave like an anionic metalloligand, we have synthesized $[Li\{Ga(SC\{O\}Ph)_4\}]$ (**1**), $[Li\{In(SC\{O\}Ph)_4\}]$ (**2**), $[Na\{Ga(SC\{O\}Ph)_4\}]$ (**3**), $[Na(MeCN)\{In(SC\{O\}Ph)_4\}]$ (**4**), $[K\{Ga(SC\{O\}Ph)_4\}]$ (**5**), and $[K(MeCN)_2\{In(SC\{O\}Ph)_4\}]$ (**6**) by reacting MX_3 and $PhC\{O\}S^-A^+$ (M = Ga(III) and In(III); X = Cl^- and NO_3^-; and A = Li(I), Na(I), and K(I)) in the molar ratio 1:4. The structures of **2**, **4**, and **6** determined by X-ray crystallography indicate that they have a one-dimensional coordination polymeric structure, and structural variations may be attributed to the change in the alkali metal ion from Li(I) to Na(I) to K(I). Crystal data for **2**·$0.5MeCN\cdot0.25H_2O$: monoclinic space group $C2/c$, $a = 24.5766(8)$ Å, $b = 13.2758(5)$ Å, $c = 19.9983(8)$ Å, $\beta = 108.426(1)°$, $Z = 8$, and $V = 6190.4(4)$ Å^3. Crystal data for **4**: monoclinic space group $P2_1/c$, $a = 10.5774(7)$ Å, $b = 21.9723(15)$ Å, $c = 14.4196(10)$ Å, $\beta = 110.121(1)°$, $Z = 4$, and $V = 3146.7(4)$ Å^3. Crystal data for **6**: monoclinic space group $P2_1/c$, $a = 12.307(3)$ Å, $b = 13.672(3)$ Å, $c = 20.575(4)$ Å, $\beta = 92.356(4)°$, $Z = 4$, and $V = 3458.8(12)$ Å^3. The thermal decomposition of these compounds indicated the formation of the corresponding AMS_2 materials.

Introduction

Very few metalloligands and macrocycles have been designed to form complexes with alkali metal ions.[1−7] We have utilized the ability of the $[M(SC\{O\}Ph)_3]^-$ anion to act as a metalloligand and reported the syntheses and characterization of compounds of the type $(NMe_4)[A\{M(SC\{O\}Ph)_3\}_2]$ (A = Na(I), K(I) and M = Cd(II), Hg(II)). In these complexes two $[M(SC\{O\}Ph)_3]^-$ anions sandwich the alkali metal ion.[8,9] The Cd(II) or Hg(II) atoms have a trigonal planar coordination environment with a MS_3 kernel, and the alkali metal ions have an octahedral AO_6 coordination environment.[8,9] Nöth et al. have reported the synthesis and characterization of the homoleptic tetrahedral anion $[In(SC\{O\}Ph)_4]^-$.[10] Our sustained interest in the chemistry of thiocarboxylates prompted us to explore the possibility of using the tetrahedral $[In(SC\{O\}Ph)_4]^-$ and $[Ga(SC\{O\}Ph)_4]^-$ anions as metalloligands to bind to various alkali metal ions. Here, we report the syntheses and structures of one-dimensional coordination polymers of the type $[A(MeCN)_x\{M(SC\{O\}Ph)_4\}]$ (A = Li(I), Na(I), K(I) and M = Ga(III), In(III); $x = 0-2$). We have also studied their potential as single-source precursors for AMS_2 compounds.

Experimental Section

General Methods. All materials were obtained commercially and used as received. The solvents were dried by allowing them to stand over 3 Å molecular sieves overnight. The preparations were carried out under a nitrogen atmosphere, and the yields are reported with respect to the metal salts. The elemental analyses were performed in the microanalytical lab in the Department of Chem-

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istry, National University of Singapore. ^{13}C{^{1}H} NMR of the compounds were recorded on a Bruker ACF 300 MHz spectrometer. The IR spectra (KBr pellet) were recorded using a Bio-Rad FTIR spectrophotometer. Thermogravimetric analyses were performed (under N_2 atmosphere) using a SDT 2980 TGA apparatus with a sample size of 5−10 mg per run.

[Li{Ga(SC{O}Ph)$_4$}]. Thiobenzoic acid (0.25 mL, 2.12 mmol) was deprotonated by LiOH (0.05 g, 2.1 mmol) in MeOH (25 mL). To this clear yellow solution of Li^{I}SC{O}Ph was added $Ga(NO_3)_3 \cdot 3H_2O$ (0.14 g, 0.45 mmol) in MeOH (10 mL). The mixture was stirred for about 1 h and the solvent evaporated under vacuum to get a creamy yellow product, which was washed several times with deionized water (to remove the $LiNO_3$ formed) and dried under vacuum. Yield: 0.21 g, (76%). Anal. Cacld for $C_{28}H_{20}O_4S_4LiGa$ (mol wt 625.39): C, 53.78; H, 3.22. Found: C, 53.35; H, 3.05. ^{13}C{^{1}H} NMR ($(CD_3)_2CO$): δ 129.46 (C$^{3/5}$ or C$^{2/6}$), 129.79 (C$^{2/6}$ or C$^{3/5}$), 133.93 (C^4), 140.81 (C^1), 197.90 (Ph*C*OS). IR data (cm^{-1}): 1597.9 (s, C═O), 1569.2 (s, C═O), 1205.6 (s, Ph−C), 921.1 (s, C−S), 648.5 (s, δ(SCO)).

[Li{In(SC{O}Ph)$_4$}]·2H$_2$O. Compound **2** was synthesized via a synthetic strategy similar to that used for synthesis of **1** except that $InCl_3 \cdot 4H_2O$ was used instead of $Ga(NO_3)_3 \cdot 3H_2O$. Yield: 79%. Anal. Cacld for $C_{28}H_{20}O_4S_4LiIn \cdot 2H_2O$ (mol wt 706.49): C, 47.60; H, 3.42. Found: C, 47.87; H, 3.56. TG weight loss: expected, 5.1%; found, 4.8% for $2H_2O$. ^{13}C{^{1}H} NMR ($(CD_3)_2CO$): δ 129.37 (C$^{3/5}$ or C$^{2/6}$), 129.62 (C$^{2/6}$ or C$^{3/5}$), 133.74 (C^4), 141.04 (C^1), 197.81 (Ph*C*OS). IR data (cm^{-1}): 1597.9 (s, C═O), 1569.2 (s, C═O), 1208.0 (s, Ph−C), 945.1 (s, C−S), 650.8 (s, δ(SCO)). Slow evaporation of the compound from MeCN solvent yielded colorless block-like single crystals of **2** which contain half a molecule of MeCN and a quarter molecule of H_2O.

[Na{Ga(SC{O}Ph)$_4$}]. Compound **3** was synthesized using a procedure identical to that of **1**, except that NaOH was used in place of LiOH. Yield: 40%. Anal. Calcd for $C_{28}H_{20}O_4S_4NaGa$ (mol wt 641.45): C, 52.43; H, 3.14. Found: C, 52.11; H, 2.69.^{13}C{^{1}H} NMR ($(CD_3)_2CO$): δ 129.58 (C$^{3/5}$ or C$^{2/6}$), 129.61 (C$^{2/6}$ or C$^{3/5}$), 133.74 (C^4), 141.71 (C^1), 198.42 (Ph*C*OS). IR data (cm^{-1}): 1594.8 (s, C═O), 1573.41 (s, C═O), 1200.9 (s, Ph−C), 907.7 (s, C−S), 647.9 (s, δ(SCO)).

[Na(MeCN){In(SC{O}Ph)$_4$}]. Dry solid NaOMe was prepared by dissolving Na (0.03 g, 1.36 mmol) in MeOH (10 mL) and removing the solvent in the flow of N_2. MeCN (15 mL) was added to obtain a suspension of NaOMe, to which PhC{O}SH (161 μL, 1.36 mmol) was added. To the resultant clear intense yellow solution of NaSC{O}Ph was added $InCl_3 \cdot 4H_2O$ (0.10 g, 0.34 mmol) in MeCN (10 mL). A clear bright yellow solution was formed, which was concentrated under vacuum until microcrystalline product started to appear. The flask was then purged with N_2 and allowed to stand in the refrigerator at 5 °C. Colorless crystals of **4**, suitable for X-ray diffraction studies, appeared the following day. An additional crop of the compound was precipitated out by addition of Et_2O (25 mL). The compound thus obtained was filtered, washed with cold MeOH (2 mL) and Et_2O (15 mL), and dried under vacuum. Combined yield: 0.21 g (90%). Anal. Calcd for $C_{28}H_{20}O_4S_4NaIn$ (mol wt 686.545) for desolvated sample: C, 48.99; H, 2.94; Na, 3.35. Found: C, 48.91; H, 2.64; Na, 3.38. ^{13}C{^{1}H} NMR ($(CD_3)_2CO$): δ 129.45 (C$^{3/5}$ or C$^{2/6}$), 129.94 (C$^{2/6}$ or C$^{3/5}$), 133.58 (C^4), 141.49 (C^1), 201.53 (Ph*C*OS). IR data (cm^{-1}): 1576.4 (s, C═O), 1199.1 (s, Ph−C), 919.3 (s, C−S), 647.9 (s, δ(SCO)).

[K{Ga(SC{O}Ph)$_4$}]·1.5H$_2$O. The compound was obtained as white powder when the synthesis was carried out as described for **1** but using KOH instead of LiOH. Yield: 0.11 g (44%). Anal. Calcd for $C_{28}H_{20}O_4S_4KGa \cdot 1.5H_2O$ (mol wt 684.54): C, 49.12; H, 3.38. Found: C, 49.47; H, 3.30. ^{13}C{^{1}H} NMR ($(CD_3)_2CO$): δ 129.49 (C$^{2/6}$ or C$^{3/5}$), 129.57 (C$^{3/5}$or C$^{2/6}$), 133.49 (C^4), 141.96 (C^1), 197.92 (PhCOS). IR data (cm^{-1}): 1575.0 (s, C═O), 1203.7 (s, Ph−C), 911.6 (s, C−S), 649.2 (s, δ(SCO)). TG weight loss: expected, 3.9%; found, 3.9%.

Table 1. Crystallographic Data and Refinement Parameters for **2**, **4**, and **6**

	2·0.25H$_2$O·0.5MeCN	**4**	**6**
chemical formula	$C_{28}H_{20}O_4S_4LiIn \cdot 0.25H_2O \cdot 0.5CH_3CN$	$C_{30}H_{23}NO_4S_4NaIn$	$C_{32}H_{26}N_2O_4S_4KIn$
fw	692.47	727.54	784.71
T, K	223	293	223
λ, Å	0.71073	0.71073	0.71073
space group	$C2/c$	$P2_1/c$	$P2_1/n$
unit cell dimens			
a, Å	24.5766(8)	10.5774(7)	12.307(3)
b, Å	13.2758(5)	21.9723(15)	13.672(3)
c, Å	19.9983(8)	14.4196(10)	20.575(4)
β, deg	108.426(1)	110.121(1)	92.356(4)
V, Å^3	6190.4(4)	3146.7(4)	3458.8(12)
Z	8	4	4
ρ, g/cm^3	1.486	1.536	1.507
μ, mm^{-1}	1.066	1.066	1.083
final R indices[a] ($I > 2\sigma(I)$)	R1 = 0.0514; wR2 = 0.1089	R1 = 0.0250; wR2 = 0.0514	R1 = 0.0349; wR2 = 0.0649
R indices (all data)	R1 = 0.0722; wR2 = 0.1166	R1 = 0.0364; wR2 = 0.0557	R1 = 0.0479; wR2 = 0.0677

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)/\sum wF_o^4]^{1/2}$.

[K(MeCN)$_2${In(SC{O}Ph)$_4$}]. K(I)SCOPh was prepared in situ by the reaction of PhCOSH (161 μL, 1.36 mmol) with KOH (0.08 g, 1.36 mmol) in 20 mL of MeOH. To this yellow solution was added $InCl_3 \cdot 4H_2O$ (0.10 g, 0.34 mmol) dissolved in MeOH (15 mL). The solvents were removed under a flow of N_2. The product was extracted into warm MeCN (15 mL), filtered, and stored in the refrigerator. Colorless crystals of X-ray diffraction quality were obtained the following day. The crystals were collected, washed with Et_2O, and dried under vacuum. Yield: 0.21 g (86%). Anal. Calcd for $C_{28}H_{20}O_4S_4KIn$ (mol wt 702.64) for the desolvated sample: C, 47.86; H, 2.87; K, 5.56. Found: C, 47.90; H, 2.84; K, 5.80. ^{13}C{^{1}H} NMR ($(CD_3)_2CO$): δ 129.44 (C$^{2/6}$ or C$^{3/5}$), 129.90 (C$^{3/5}$ or C$^{2/6}$), 133.47 (C^4), 141.60 (C^1), 201.14 (PhCOS). IR data (cm^{-1}): 1552.0 (s, C═O), 1199.1 (s, Ph−C) 938.6 (s, C−S), 651.1 (m, δ(SCO)).

X-ray Crystallography. The diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a Mo Kα sealed tube. The program SMART[11] was used for collecting frames of data, indexing reflection and determination of lattice parameters, SAINT[11] for integration of the intensity of reflections and scaling. SADABS[12] was used for absorption correction and SHELXTL[13] for space group and structure determination and least squares refinements on F^2. The single crystals of **2**, **4**, and **6** were obtained by slow evaporation of MeCN. Compound **2** crystallizes with 0.25 water molecule and 0.5 MeCN solvent molecule while **4** and **6** crystallize with one and two MeCN solvate molecules, respectively. The relative stoichiometric composition of the solvents in **2** was based on the relative electron densities found in the difference Fourier routine. Further, the top three peaks in the final difference Fourier map with electron densities 0.94−0.85 e Å^{-3} were associated with In(1) atom while the residual electron densities (<0.72 e Å^{-3}) found near the solvent region were featureless. The relevant crystallographic data and refinement details are shown in Table 1.

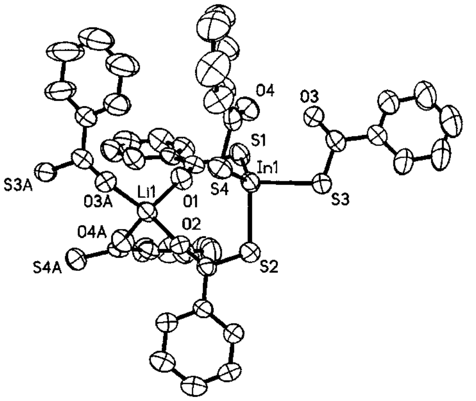

Figure 1. A thermal ellipsoid plot (50% probability) showing the coordination geometry at Li(I) and In(III) in **2**.

Results and Discussion

Synthesis. The compounds ([Li{Ga(SC{O}Ph)$_4$}] (**1**), [Li{In(SC{O}Ph)$_4$}] (**2**), [Na{Ga(SC{O}Ph)$_4$}] (**3**), [Na(MeCN){In(SC{O}Ph)$_4$}] (**4**), [K{Ga(SC{O}Ph)$_4$}] (**5**), and [K(MeCN)$_2${In(SC{O}Ph)$_4$}] (**6**) were prepared by a simple reaction between the metal salts and appropriate amounts of the corresponding alkali metal salt of thiobenzoate anions in MeCN solvent as shown in eq 1. The yields are moderate

$$MX_3 + 4C_6H_5COS^-A^+ \rightarrow [A\{M(SC\{O\}Ph)_4\}] + 3AX \quad (1)$$

$$M = Ga(III), In(III); A = Li(I), Na(I), K(I)$$

to quantitative. The compounds are insoluble in CH_2Cl_2 or $CHCl_3$ but soluble in MeCN and $(Me)_2CO$ and sparingly soluble in MeOH. The compounds are found to be very stable, and no apparent decomposition occurred when the compounds were left at room temperature. The structural characterization of these compounds mainly depends on X-ray crystallography as the usual spectroscopic techniques are not informative. Thermogravimetry and the elemental analysis of **2** and **5** suggested the presence of lattice water.

Structural Descriptions of 2, 4, and 6. Compounds **2**, **4**, and **6** are one-dimensional coordination polymers in which the [In(SC{O}Ph)$_4$]$^-$ anion acts like a multidentate ligand to bind the alkali metal cations. Detailed structural descriptions are given in the following sections.

Structure of [Li{In(SC{O}Ph)$_4$}]·0.25H$_2$O·0.5MeCN. The structure of **2** is shown in Figure 1, and selected bond lengths and angles are displayed in Table 2. **2** consists of tetrahedral [In(SC{O}Ph)$_4$]$^-$ units in which the thiobenzoate anion binds to the In(III) mainly through the sulfur donor site; however, the distance between In(1) and the oxygen atoms of the thiobenzoate anions, namely, O(1), O(2), O(3), and O(4), are 2.648(3), 3.379(3), 3.364(3), and 2.713(4) Å, respectively. All these distances are shorter than the sum of their van der Waals radii (3.4 Å).[14] Thus the In(1) metal atom could be considered as having 4 + 4 coordination number. Each Li(I) is bonded to four carbonyl oxygen atoms, two from each [In(SC{O}Ph)$_4$]$^-$ unit to have tetrahedral geometry with O$_4$ donor set. The anionic [In(SC{O}Ph)$_4$]$^-$ units act as bridging ligands and interact with Li(I) ions in the solid state to generate a polymeric structure. A segment of the polymeric compound **2** is shown in Figure 2. The polymeric chains are packed along the *b* axis, and it appears that there is no strong interaction between the adjacent polymeric strands. Incidentally, **2** is the second lithium thiocarboxylate compound to be structurally characterized, the first compound being the dimeric [(tmen)LiSC{O}Ph]$_2$.[15]

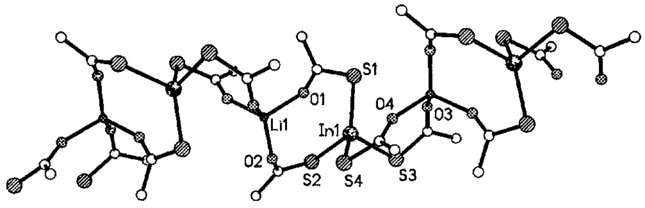

Figure 2. A segment of the one-dimensional coordination polymeric structure in **2**.

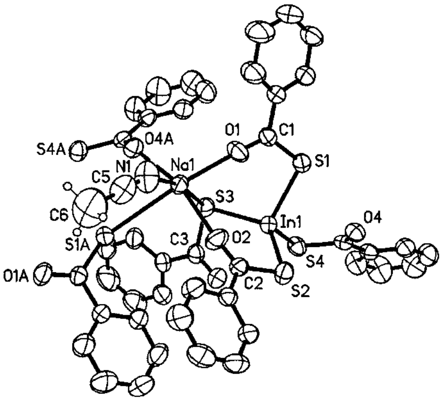

Figure 3. An ORTEP diagram illustratingi the coordination sphere at Na(I) and In(III) in **4**.

Structure of [Na(MeCN)In(SC{O}Ph)$_4$]. A portion of the polymeric structure of **4** is illustrated in Figure 3, and selected bond distances and angles are listed in Table 3. Each In(III) is bonded to sulfur atoms of the four thiobenzoate anions. The In···O distances are less than the sum of their van der Waals radii, and hence In(1) has a 4 + 4 coordination geometry as discussed for **2**. The broad range of S−In−S angles, 99.75(2)−127.25(2)°, clearly indicates this distortion. The In−S distances are equal except for In(I)−S(2), 2.462 Å.

The sulfur and oxygen atoms of the thiobenzoato ligands are further bonded to Na(I) to form a one-dimensional polymer as shown in Figure 4. All the polymeric strands are arranged parallel to each other in the *c* direction. The Na(I) has distorted octahedral geometry with a S$_2$O$_3$N$_1$ donor set and is surrounded by two [In(SC{O}Ph)$_4$]$^-$ anions and an acetonitrile ligand. One [In(SC{O}Ph)$_4$]$^-$ anion acts as a claw-like tridentate ligand in which two carbonyl oxygen atoms, O(1) and O(2), and a sulfur atom, S(3), are bonded

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**·0.5MeCN·0.25H$_2$O[a]

		Bond Distances			
In(1)−S(1)	2.470(1)	In(1)−S(2)	2.5015(13)	In(1)−S(3)	2.503(1)
In(1)−S(4)	2.475(1)	S(1)−C(1)	1.718(5)	O(1)−Li(1)	1.943(8)
O(2)−Li(1)	1.876(8)	O(3)−Li(1)^a	1.880(9)	O(4)−Li(1)^a	1.947(8)
		Bond Angles			
S(1)−In(1)−S(2)	111.27(5)	S(1)−In(1)−S(3)	105.08(5)	S(1)−In(1)−S(4)	131.25(5)
S(4)−In(1)−S(2)	103.75(5)	S(4)−In(1)−S(3)	108.19(5)	S(2)−In(1)−S(3)	89.38(5)
O(2)−Li(1)−O(1)	102.6(4)	O(3)^b−Li(1)−O(1)	107.6(4)	O(2)−Li(1)−O(3)^b	129.4(5)
O(2)−Li(1)−O(4)^b	106.6(4)	O(3)^b−Li(1)−O(4)^b	101.6(4)	O(1)−Li(1)−O(4)^b	107.7(4)

[a] Symmetry transformations used to generate equivalent atoms: a $-x + {}^3/_2, y + {}^1/_2, -z + {}^3/_2$; b $-x + {}^3/_2, y - {}^1/_2, -z + {}^3/_2$.

Table 3. Selected Bond Lengths and Angles for **4**[a]

		Bond Distances			
In(1)−S(1)	2.486(1)	In(1)−S(2)	2.462(1)	In(1)−S(3)	2.486(1)
In(1)−S(4)	2.486(1)	O(1)−Na(1)	2.291(2)	O(2)−Na(1)	2.269(2)
Na(1)−O(4)^b	2.315(1)	Na(1)−S(1)^b	3.141(1)	S(3)−Na(1)	3.073(1)
Na(1)−N(1)	2.377(2)				
		Bond Angles			
S(2)−In(1)−S(1)	112.68(2)	S(3)−In(1)−S(1)	104.26(2)	S(2)−In(1)−S(3)	127.25(2)
S(2)−In(1)−S(4)	107.45(2)	S(3)−In(1)−S(4)	99.75(2)	S(1)−In(1)−S(4)	102.12(2)
In(1)−S(1)−Na(1)^a	103.98(2)	In(1)−S(3)−Na(1)	87.92(2)	O(2)−Na(1)−O(1)	86.46(6)
O(2)−Na(1)−O(4)^b	155.77(7)	O(1)−Na(1)−O(4)^b	106.29(6)	O(2)−Na(1)−S(3)	77.20(5)
O(1)−Na(1)−S(3)	77.21(4)	O(4)^b−Na(1)−S(3)	85.50(4)	N(1)−Na(1)−S(3)	168.06(7)
N(1)−Na(1)−S(1)^b	81.68(6)	S(3)−Na(1)−S(1)^b	86.82(3)	C(5)−N(1)−Na(1)	146.5(2)
N(1)−C(5)−C(6)	178.4(4)				

[a] Symmetry transformations used to generate equivalent atoms: a $x, -y + {}^1/_2, z - {}^1/_2$; b $x, -y + {}^1/_2, z + {}^1/_2$.

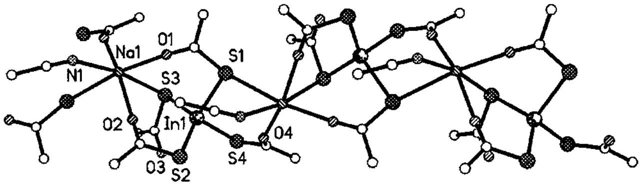

Figure 4. A portion of the one-dimensional coordination polymeric structure in **4**.

to Na(I) in a *facial* manner and the second [In(SC{O}Ph)$_4$]$^-$ anion is chelating through O(4) and S(1). The octahedral core is completed by the N(1) of an acetonitrile ligand. The Na−S distances, 3.073(1) and 3.141(1) Å, are in the upper range of the reported Na−S distances (2.684−3.136 Å).[16] Interestingly, not many heterometallic complexes containing sulfur donor ligands with alkali metals have been reported.[17−19]

The Na−O and Na−N distances are unexceptional,[8,9,14,20] but the Na(1)−N(1)−C(5) angle, 146.5(2)°, deviates significantly from linearity. Though the majority of compounds in the literature show a M−N−C angle ranging from 164° to 180°,[16] there are quite a few compounds which exhibit a M−N−C angle of 140−158°.[21−23] Highly distorted octahedral geometry at Na(1) is implied from the bond angles. The interplanar angle between the C−C{O}S atoms and the phenyl ring of the thiocarboxylate anion varies from 2.8(1)° to 21.56(8)°. From the thiobenzoato ligand point of view, one has a μ_3-S_2,O bonding mode, two are acting as bidentate ligands bridging In(III) and Na(I) metal ions with μ-S,O bonding, and the fourth one, S(3), is in μ bridging mode. The oxygen atom O(4) is the only donor site not involved in bonding.

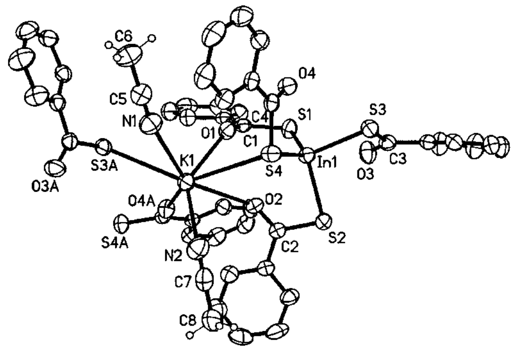

Figure 5. A perspective thermal ellipsoid plot with 50% probability, showing the coordination environment around K(I) and In(III) in **6**.

Structure of [(MeCN)$_2$K{In(SC{O}Ph)$_4$}]. Compound **6** is also a coordination polymer, having the formula [(MeCN)$_2$K{In(SC{O}Ph)$_4$}]. A portion of the polymeric structure of **6** showing the details of the geometries around the metal ions and PhC{O}S$^-$ ligands is illustrated in Figure 5, and selected bond lengths and angles are displayed in Table 4. The compound basically consists of [In(SC{O}Ph)$_4$]$^-$ and K(MeCN)$_2$ repeating units similar to **2** and **4**, but the In−S distances fall in a wider range, 2.453(1)−2.512(1) Å.

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for **6**^{a}

		Bond Lengths			
In(1)−S(1)	2.453(1)	In(1)−S(2)	2.512(1)	In(1)−S(3)	2.508(1)
In(1)−S(4)	2.487(1)	K(1)−O(1)	2.693(2)	K(1)−O(2)	2.783(2)
K(1)−O(4)^a	2.738(2)	K(1)−S(4)	3.664(1)	K(1)−S(3)^a	3.733(1)
K(1)−N(1)	2.821(3)	K(1)−N(2)	2.841(3)		
		Bond Angles			
S(1)−In(1)−S(2)	111.88(3)	S(1)−In(1)−S(3)	106.62(2)	S(1)−In(1)−S(4)	127.80(3)
S(3)−In(1)−S(2)	99.97(3)	S(4)−In(1)−S(2)	103.56(2)	S(4)−In(1)−S(3)	103.39(2)
O(1)−K(1)−O(4)^a	92.58(6)	O(1)−K(1)−O(2)	66.17(5)	O(4)^a−K(1)−O(2)	82.80(5)
O(1)−K(1)−N(1)	87.72(7)	O(4)^a−K(1)−N(1)	129.11(6)	O(2)−K(1)−N(1)	140.83(7)
O(1)−K(1)−N(2)	137.39(7)	O(4)^a−K(1)−N(2)	103.68(7)	O(2)−K(1)−N(2)	77.01(7)
N(1)−K(1)−N(2)	109.95(8)	O(1)−K(1)−S(4)	65.67(4)	O(4)^a−K(1)−S(4)	142.67(4)
O(2)−K(1)−S(4)	61.04(4)	N(1)−K(1)−S(4)	82.12(5)	N(2)−K(1)−S(4)	78.36(6)
O(1)−K(1)−S(3)^a	91.02(4)	O(4)^a−K(1)−S(3)^a	60.12(4)	O(2)−K(1)−S(3)^a	135.97(4)
N(1)−K(1)−S(3)^a	68.99(5)	N(2)−K(1)−S(3)^a	131.27(6)	S(4)−K(1)−S(3)^a	143.76(2)
In(1)−S(3)−K(1)^b	83.14(2)	In(1)−S(4)−K(1)	90.95(2)		

^{a} Symmetry transformations used to generate equivalent atoms: a $-x + {}^3/_2$, $y + {}^1/_2$, $-z + {}^1/_2$; b $-x + {}^3/_2$, $y - {}^1/_2$, $-z + {}^1/_2$.

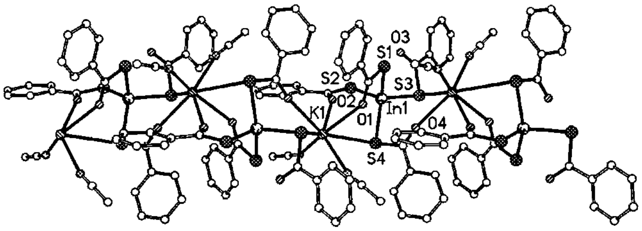

Figure 6. A fragment of the polymeric structure in **6**.

The In(1) metal atom is bonded to four sulfur donor sites from the thiobenzoate anions and weakly bonded to four the carbonyl oxygen atoms. As a consequence the S−In−S angles, 99.97(3)−127.80(3)°, show large deviation from the ideal tetrahedral angle. The [In(SC{O}Ph)$_4$]$^-$ anion acts as a multidentate bridging ligand and interacts with two different K(I) ions in the solid state to generate the 1D polymeric structure. One [In(SC{O}Ph)$_4$]$^-$ unit binds to the potassium as a tridentate ligand through two carbonyl oxygen atoms, O(1) and O(2), and one sulfur atom, S(4). The other In(SC{O}Ph)$_4$ unit binds through one sulfur, S(1), and one oxygen atom, O(4). There are two acetonitrile solvent molecules coordinating to the potassium ion. Thus, the potassium ion is seven coordinated with a $S_2O_3N_2$ donor set. The coordination geometry around K(1) may be described as highly distorted pentagonal bipyramidal geometry. A view of the polymeric structure of **6** is shown in Figure 6.

Very few heterometallic aggregates containing sulfur donor ligands with potassium have been reported.[24,25] The K−S distances, 2.664(1) and 3.733(1) Å, are longer than those observed for [(C_6H_5C{O}SK)], [(2-OMe-C_6H_4C{O}SK)], and [(4-OMe-C_6H_4C{O}SK)] (3.238(2)−3.483(1) Å)[26] and other related compounds in the literature (3.039−3.485 Å).[16] The thiobenzoato ligand adapts μ_3-*S$_2$,O*, μ_2-*S,O*, and μ_2-*S* bonding bonds to form the coordination polymer. The carbonyl oxygen O(3) is the only potential bonding site not involved in bonding in **6**.

Changing the alkali metal atom from Li(I) to Na(I) to K(I) is accompanied by changes in the coordination modes of the metalloligand, [In(SC{O}Ph)$_4$]$^-$. In **2**, the thiobenzoate anion utilizes the μ-*S,O* bonding mode to bond to the Li(I) metal atom while, in **4** and **6**, μ_3-*S$_2$,O*, μ-*S,O*, and μ-*S* bonding modes are used to bind to Na(I) and K(I) cations. Another striking difference between **2**, **4**, and **6** is the coordination number of the alkali metal atom. In **2**, the Li(I) metal ion is four coordinate while in **4** and **6** the coordination numbers are six and seven, respectively. This could, obviously, be attributed to the size of the alkali metal ion. The distortion of the metalloligand [In(SC{O}Ph)$_4$]$^-$ from the ideal tetrahedral symmetry (as inferred from the S−In−S angles) is greater in **2**. However, **4** and **6** are distorted to a similar extent. There seems to be no significant influence in the distortion of the geometry of the [In(SC{O}Ph)$_4$]$^-$ anion upon replacement of sodium by potassium. Weak interactions between In and O atoms exist in all three compounds. Indium metal atom is 4 + 4 coordinated, if these weak interactions were to be taken into account. The nonbonding distances between the alkali metal atom and the indium metal atom are shorter than the sum of their van der Waals radii in **4** and **6**, while the distance is slightly longer in **2**.

Thermogravimetry and Pyrolysis. The compounds **1**−**6** described here have correct stoichiometry of the metals as precursors for AMS_2 compounds. Materials of the type ABX_2 (A= alkali metal ion, B = a trivalent cation, X = O, S, Se) are known to be wide band gap semiconductors[27−31] and have nonlinear optical properties.[32] Incorporation of $NaInS_2$ into a $CuInS_2$ layer seems to improve the cell performance.[33] The preparation of these materials is through typical solid state synthetic methods involving temperatures as high as 900 °C.[34−36] The thermal decomposition of **1**−**6** has been

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Table 5. TGA Results for **1**−**6**

compound	TG results temp range (°C)	 resid wt obsd (calcd) (%)	expected prod. of decomp
1	171−515	22.6 (22.5)	$LiGaS_2$
2·$2H_2O$	50−147	95.2 (94.9)	anhydrous **2**
	186−518	30.2 (26.3)	$LiInS_2$
3	203−557	25.2 (24.5)	$NaGaS_2$
4	222−549	32.5 (29.4)	$NaInS_2$
5·$1.5H_2O$	50−135	96.1 (96.1)	anhydrous **5**
	195−541	28.7 (25.3)	$KGaS_2$
6	220−528	35.9 (31.0)	$KInS_2$

investigated using TG to explore the usage of these compounds as single-source precursors for AMS_2 materials.

TG weight loss experiments in N_2 atmosphere show that the inception of weight loss occurs in the range 172−222 °C as shown in the Table 5. Their thermal stability follows the order **1** < **2**; **3** < **4**; and **5** < **6**. The compounds decompose in unresolved multiple steps in the temperature region 172−557 °C. The final products of decomposition at the plateau are expected to be due to the formation of AMS_2 compounds. However, the residual weight losses observed in the TG experiments are slightly higher than the calculated residual weights for AMS_2 compounds for **2**, **5**, and **6** (Table 5). The excess residual weight may be due to unremoved side products of decomposition. However, the weight of the residue observed in our preliminary results of the pyrolysis studies carried out under low pressure (0.5 Torr) matched well with the expected residual weight based on the formation of AMS_2 compounds, thus providing support for the observed excess weight in TG experiments.

The single-source molecular precursor method appears to be an attractive route to prepare AMS_2 compounds since the traditional synthetic method requires temperatures as high as 900 °C. Further investigations on the characterization of the final residue of thermal decomposition are in progress, and the results will be published elsewhere.

Summary

We have shown that $[M(SC\{O\}Ph)_4]^-$ can be used as a metalloligand to bind to various alkali metal ions, and isolated six new compounds of the type $[A(MeCN)_2\{M(SC\{O\}Ph)_4\}]$ (A = Li(I), Na(I), and K(I); M = Ga(III) and In(III); $x = 0-2$). The anion $[M(SC\{O\}Ph)_4]^-$ acts like a multidentate ligand and forms one-dimesional coordination polymers, as shown by X-ray crystallography for **2**, **4**, and **6**. Such alkali metal containing compounds of group 13 metal compounds have been the subject of recent interest.[37] Thermal decomposition of these compounds suggests the formation of the corresponding AMS_2 materials. On the basis of our investigations, **1**−**6** could be used as potential precursors to the ternary AMS_2 materials.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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