Inorg. Chem. **2006**, *45*, 8258–8263

Inorganic Chemistry
Article

Syntheses and Structures of $[M\{In(SC\{O\}Ph)_4\}_2]$ (M = Mg and Ca): Single Molecular Precursors to MIn_2S_4 Materials

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Received June 5, 2006

The compounds $[Mg\{In(SC\{O\}Ph)_4\}_2]$ (**1**) and $[Ca(H_2O)_x\{In(SC\{O\}Ph)_4\}_2]\cdot yH_2O$ ($x = 0$, $y = 1$, **2** major product; $x = 1$, $y = 0$, **2a** minor product; $x = 2$, $y = 2$, **2b** minor product) have been synthesized by reacting $InCl_3$ and $M(SC\{O\}Ph)_2$ (M = Mg and Ca) prepared in situ in the molar ratio 1:2. The structures of **1**, **2a**, and **2b** have been determined by X-ray crystallography. The structure of **1** consists of two tetrahedral $[In(SC\{O\}Ph)_4]^-$ anions sandwiching the Mg^{II} metal ions through six carbonyl O atoms. The coordination geometry at the Mg^{II} metal atom is distorted octahedral with an O_6 donor set. The structures of **2a** and **2b** consist of two $[In(SC\{O\}Ph)_4]^-$ anions sandwiching the Ca^{II} metal ion through five and four carbonyl O atoms, and the octahedral coordination at the Ca^{II} centers is completed by one and two aqua ligands, respectively. Two aqua ligands and two lattice water molecules form a H-bonded water chain in the channel created by $[Ca\{In(SC\{O\}Ph)_4\}_2]$ molecules in the crystal structure of **2b**. The thermal decomposition of **1** and **2** indicated the formation of the corresponding MIn_2S_4 materials, and this was confirmed by X-ray powder diffraction patterns.

Introduction

For more than a decade, we have been interested in the development of the chemistry of metal thiocarboxylate complexes. The interest derives from their fascinating structural chemistry[1−4] and from the fact that many of them can be used as single molecular precursors for the low-temperature synthesis of bulk metal sulfides, thin films, and nanoparticles.[5−8] Monothiocarboxylates ($RC\{O\}S^-$) represent an interesting class of ligands with both hard and soft donors.[1] These donor sites enable the incorporation of hard and soft metal centers into a coordination compound, as illustrated by the clawlike $[M(SC\{O\}Ph)_3]^-$ metalloligand complexes $(Me_4N)[A\{M(SC\{O\}Ph)_3\}_2]$ ($A = Na^I$ and K^I and $M = Cd^{II}$ and Hg^{II}).[2] In these complexes, two $[M(SC\{O\}Ph)_3]^-$ anions sandwich an alkali metal ion. The Cd^{II} or Hg^{II} atoms have a trigonal-planar MS_3 coordination environment, and the alkali-metal ions have an octahedral AO_6 core.[2] Subsequently, we have studied the tetrahedral $[In(SC\{O\}Ph)_4]^-$ anions as metalloligands to bind to various alkali-metal ions to form $[A(MeCN)_x\{M(SC\{O\}Ph)_4\}]$ ($A = Li^I$, Na^I, and K^I and $M = Ga^{III}$ and In^{III}; $x = 0-2$), which are one-dimensional coordination polymers.[9] In a continuation of our investigations on the chemistry of metal thiocarboxylate compounds, we report Mg^{II} and Ca^{II} complexes of $[In(SC\{O\}Ph)_4]^-$ anions in this paper. The syntheses and structures of $[Mg\{In(SC\{O\}Ph)_4\}_2]$ (**1**) and $[Ca(H_2O)_x\{In(SC\{O\}Ph)_4\}_2]\cdot yH_2O$ ($x = 0$, $y = 1$, **2**; $x = 1$, $y = 0$, **2a**; $x = 2$, $y = 2$, **2b**) are described. Such $II-III_2-VI_4$ materials have potential

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Table 1. Crystallographic Data and Refinement Parameter for **1**, **2a**, and **2b**

	1	**2a**	**2b**[a]
chemical formula	$C_{56}H_{40}In_2Mg\,O_8S_8$	$C_{56}H_{42}CaIn_2O_9S_8$	$C_{56}H_{48}CaIn_2O_{12}S_8$
fw	1351.40	1383.58	1439.24
cryst syst	monoclinic	monoclinic	tetragonal
T, °C	−50	−50	−50
λ, Å	0.710 73	0.710 73	0.710 73
space group	$P2_1/c$	$P2_1/c$	$P4_12_12$
a, Å	19.0741(7)	13.811(3)	19.5247(7)
b, Å	11.1258(4)	30.544(7)	19.5247(7)
c, Å	26.6374(10)	16.527(4)	15.8951(7)
β, deg	90.422(2)	112.998(6)	90
V, Å^3	5652.7(4)	6418(3)	6059.4(4)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.588	1.434	1.578
μ, mm^{-1}	1.175	1.108	1.180
final R indices[b] [$I > 2\sigma(I)$]	R1 = 0.0529	R1 = 0.1288	R1 = 0.0314
	wR2 = 0.1382	wR2 = 0.3291	wR2 = 0.0689
R indices (all data)	R1 = 0.0643	R1 = 0.1598	R1 = 0.0338
	wR2 = 0.1432	wR2 = 0.3480	wR2 = 0.0698

[a] Flack parameter, −0.04(2). [b] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)/\sum wF_o^4]^{1/2}$.

Table 2. Selected Bond Distance (Å) and Angle (deg) Ranges in **1**, **2a**, and **2b**

	1 (M = Mg)	**2a** (M = Ca)	**2b** (M = Ca)
		Bond Distance Range	
In−S	2.453(2)−2.512(2)	2.441(6)−2.514(4)	2.461(1)−2.488(1)
M−O	2.006(4)−2.060(4)	2.28(1)−2.32(1)	2.312(3)−2.363(3)
S−C	1.716(6)−1.755(6)	1.70(2)−1.76(2)	1.742(4)−1.763(4)
O−C	1.213(6)−1.234(6)	1.21(2)−1.24(2)	1.218(4)−1.232(4)
		Bond Angle Range	
S−In−S	88.75(5)−124.23(8)	92.5(2)−128.2(1)	106.02(3)−108.71(4)
cis O−M−O	85.6(2)−93.5(2)	79.4(4)−103.7(4)	78.2(2)−122.9(1)
trans O−M−O	174.7(2)−176.9(2)	164.4(4)−170.3(3)	156.7(1)−172.8(2)
C−S−In	85.9(2)−113.9(2)	87.8(5)−109.0(5)	91.3(1)−100.9(1)
C−O−M	155.6(4)−168.8(4)	137.2(9)−164.7(9)	161.1(3)−170.0(3)

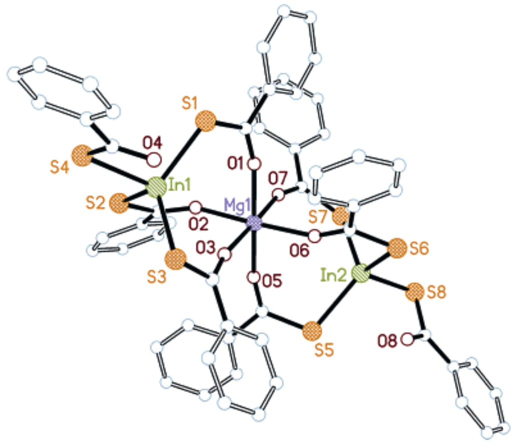

Figure 1. Molecular structure of **1** with its numbering scheme.

applications in optoelectronics.[10] These compounds have also been investigated as single-source precursors for MIn_2S_4 materials. The literature on the heterobimetallic compounds containing In^{III} is limited. A Cambridge Structural Database (version 5.27, May 2006) search reveals that there are only four structures containing both Mg^{II} and In^{III}.[11−14] In one structure, the two metals are bridged by fluorine atoms[11] and the other three are salts. However, there is no report on the structures containing Ca^{II} and In^{III}, and hence compound **2** and its hydrated forms are unique, and probably they represent the first series of heterobimetallic compounds containing both Ca^{II} and In^{III}.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry N_2 via standard Schlenk techniques. The starting materials thiobenzoic acid (Alfa Aesar, 90%), MgO (Merck, 97%), $Ca(OH)_2$ (GCE, 97%), and $InCl_3$ (Aldrich, 98%) were obtained commercially and used as received. The yields are reported with respect to In^{III} salts. The elemental analyses were performed in the microanalytical laboratory in the Department of Chemistry, National University of Singapore. $^{13}C\{^1H\}$ NMR spectra of the compounds were recorded on a Bruker ACF 300-MHz spectrometer. Thermogravimetric (TG) analyses were performed (under a N_2 atmosphere) using a SDT 2960 TGA apparatus with a sample size of 8−10 mg per run. X-ray powder diffraction patterns were obtained using a

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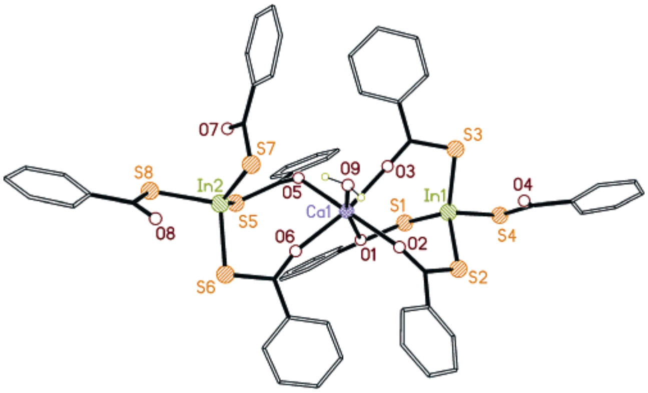

Figure 2. Ball-and-stick diagram showing the molecular structure of **2a**.

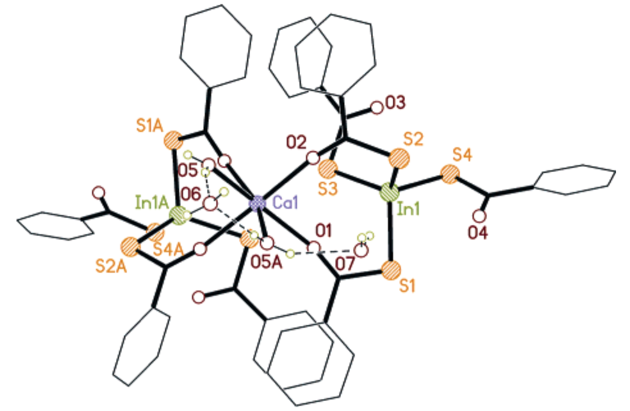

Figure 3. Ball-and-stick diagram showing the molecular structure of **2b**.

Bruker D5005 X-ray diffractometer equipped with Cu Kα radiation. The accelerating voltage and current were 40 kV and 40 mA, respectively. The IR spectra (KBr pellet) were recorded using a FTS 165 Bio-Rad FTIR spectrometer in the range 4000−400 cm^{-1}.

[Mg{In(SC{O}Ph)$_4$}$_2$] (1). Thiobenzoic acid (0.25 mL, 2.12 mmol) was deprotonated by MgO (0.043 g, 1.06 mmol) in MeOH (10 mL). To this yellow turbid solution of $Mg(SC\{O\}Ph)_2$ was added $InCl_3$ (0.120 g, 0.53 mmol) in MeOH (10 mL). The mixture was stirred for about 30 min, the solvent was evaporated under vacuum to get a creamy yellow product, which was washed with diethyl ether, and the residue was extracted into dichloromethane. The CH_2Cl_2 filtrate was concentrated and layered with hexane. A white crystalline precipitate started forming almost immediately. The flask was then allowed to stand in the refrigerator at 5 °C. Colorless needlelike crystals of **1** appeared the following day, which were suitable for X-ray diffraction studies. Yield: 0.24 g (68%). Anal. Calcd for **1**, $C_{56}H_{40}In_2MgO_8S_8$ (mol wt 1351.40): C, 49.77; H, 2.98; S, 18.98. Found: C, 49.45; H, 2.79; S, 19.22. $^{13}C\ \{^1H\}$ NMR ($CDCl_3$): δ 128.2 (*m-C*), 128.9 (*o-C*), 133.8 (*p-C*), 137.8 (*ipso-C*), 209.1 (Ph*C*OS). IR data (cm^{-1}): 1589 (s, C═O), 1568 (s, C═O), 1212 (s, Ph−C), 932 (s, C−S), 652 (s, δ(SCO)). ESI-MS (acetone) at 50 °C: *m*/*z* 663.2 ($[In(SC\{O\}Ph)_4]^-$, 15%), 137.4 ($PhC\{O\}S^-$, 100%).

[Ca(H$_2$O)$_x${In(SC{O}Ph)$_4$}$_2$]·*y*H$_2$O ($x = 0$, $y = 1$, **2**; $x = 1$, $y = 0$, **2a**; $x = 2$, $y = 2$, **2b**) can be obtained under different experimental conditions. Compound **2** was synthesized via a synthetic strategy similar to that of **1** except that $Ca(OH)_2$ was used instead of MgO. Colorless blocklike crystals of **2** were obtained as the major product, but it became opaque after 1 day in the mother liquid. However, very long thin rodlike crystals of **2a** were obtained as a minor product along with **2**, which were suitable for single-crystal X-ray diffraction experiments. Yield of **2**: 58%. Anal. Calcd for **2**, $C_{56}H_{42}CaIn_2O_9S_8$ (mol wt 1385.19): C, 48.56; H, 3.06; S, 18.52. Found: C, 48.20; H, 3.53; S, 18.05. $^{13}C\ \{^1H\}$ NMR ($CDCl_3$): δ 128.2 (*m-C*), 129.0 (*o-C*), 133.7 (*p-C*), 138.1 (*ipso-C*), 209.0 (Ph*C*OS). IR data (cm^{-1}): 1587 (s, C═O), 1553 (s, C═O), 1210 (s, Ph−C), 937 (s, C−S), 652 (s, δ(SCO)). ESI-MS (acetone) at 50 °C: *m*/*z* 663.1 ($[In(SC\{O\}Ph)_4]^-$, 65%), 137.3 ($PhC\{O\}S^-$, 100%). TG weight loss: expected, 1.3%; found, 1.2%. Anal. Calcd for **2a**, $C_{56}H_{42}CaIn_2O_9S_8$ (mol wt 1385.19): C, 48.56; H, 3.06; S, 18.52. Found: C, 48.08; H, 3.65; S, 18.36. Another minor product **2b** was obtained as follows. After the reaction mixture was stirred for about 30 min, the solvent was evaporated under vacuum to get a creamy yellow product, which was washed several times with MeOH and deionized water. The MeOH filtrate afforded single crystals of $[Ca(H_2O)_2\{In(SC\{O\}Ph)_4\}_2]\cdot 2H_2O$. Anal. Calcd for **2b**, $C_{56}H_{48}CaIn_2O_{12}S_8$ (mol wt 1439.24): C, 46.73; H, 3.36. Found: C, 45.10; H, 4.29. Because of the hygroscopic nature, the elemental analysis is not very accurate and not consistent with the proposed formula for **2b**.

X-ray Crystallography. Single crystals were obtained during the synthesis. The diffraction experiments were carried out at −50 °C on a Bruker SMART CCD diffractometer with a Mo Kα sealed tube. The program *SMART*[15] was used for collecting frames of data, indexing reflection, and determining lattice parameters, *SAINT*[15] for integration of the intensity of reflections and scaling, *SADABS*[16] for absorption correction, and *SHELXTL*[17] for space group and structure determination and least-squares refinements on F^2. One of the thiobenzoate ligands in **2a** was found to be disordered. Two disordered phenyl rings (70:30) were resolved. The positional and isotropic thermal parameters of all of the H atoms of the water molecules in **2b** were refined in the model. The relevant crystallographic data and refinement details are compiled in Table 1, and selected bond distance and angle ranges are given in Table 2.

Results and Discussion

Synthesis. Compounds **1** and **2** were prepared by a simple reaction between the metal salts and appropriate amounts of the corresponding alkaline-earth metal salt of thiobenzoate anions prepared in situ in a MeOH solvent, as shown in eqs 1 and 2.

$$MO\ \text{or}\ M(OH)_2 + 2PhC\{O\}SH \rightarrow M(SC\{O\}Ph)_2 + xH_2O \quad (x = 1\ \text{or}\ 2) \quad (1)$$

$$4M(SC\{O\}Ph)_2 + 2InCl_3 \rightarrow [M\{In(SC\{O\}Ph)_4\}_2] + 3MCl_2 \quad (M = Mg\ \text{and}\ Ca) \quad (2)$$

The compounds are soluble in CH_2Cl_2, $CHCl_3$, and $(Me)_2CO$ but insoluble in MeCN, MeOH, and EtOH. The desolvated compounds are found to be very stable, and no apparent decomposition occurred when they were left at room temperature in air. Compound **2** with a variable number of water molecules has been isolated. Upon prolonged exposure to humid air, **2a** and **2b** with more water in the lattice and

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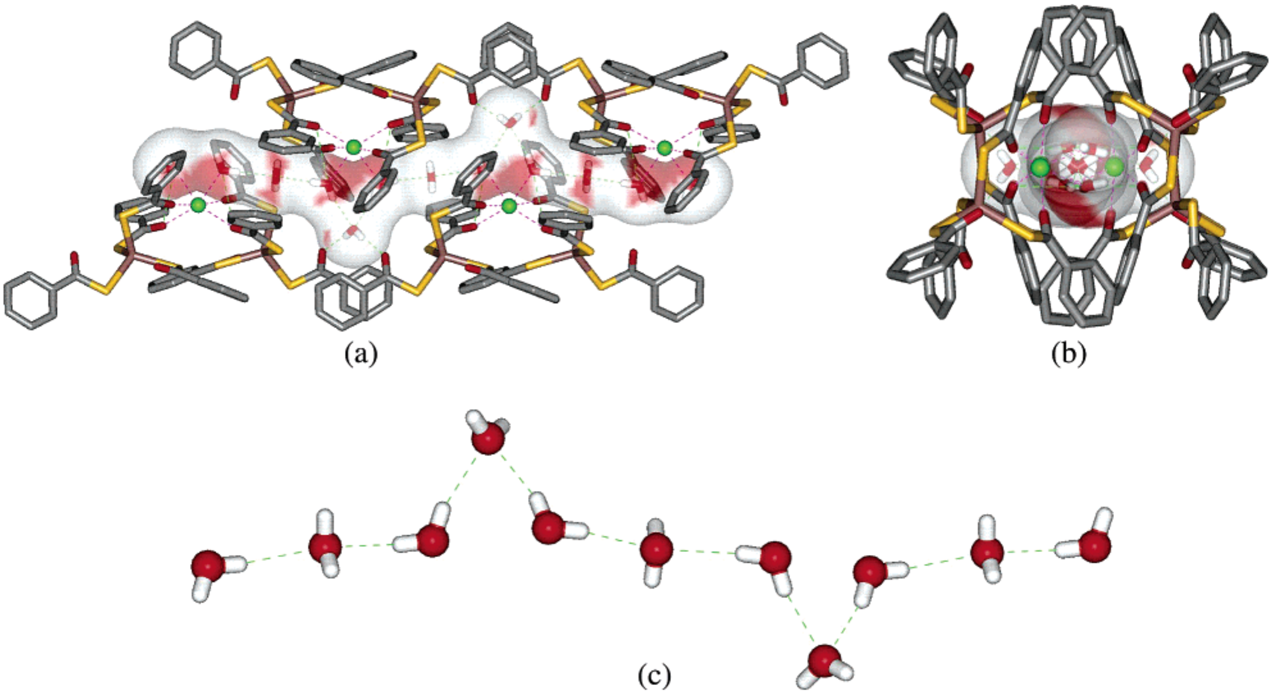

Figure 4. (a and b) Two views of the H-bonded water chain inside the channel created by [Ca{In(SC{O}Ph)$_4$}$_2$] in **2a**. Color code: red, O; green, Ca^{II}; brown, In^{III}; yellow, S; black, C; white, H. (c) Perspective view of the water chain. All C−H hydrogen atoms are omitted for clarity.

Table 3. Selected H-Bonding Parameters in **2b**[a]

D−H···A	d(D−H)	d(H···A)	∠DHA	d(D···A)
O5−H5A···O7[a]	0.77(2)	2.12(3)	153(6)	2.830(3)
O5−H5B···O6[b]	0.78(2)	2.01(2)	165(3)	2.772(5)
O6−H6···O4	0.76(2)	2.07(1)	173(4)	2.830(3)
O7−H7···S2	0.78(2)	2.71(3)	150(2)	3.407(4)

[a] Symmetry operators: a, $-x + 1, -y + 1, z + {}^1/_2$; b, $-x + 1, -y + 1, z + {}^1/_2$.

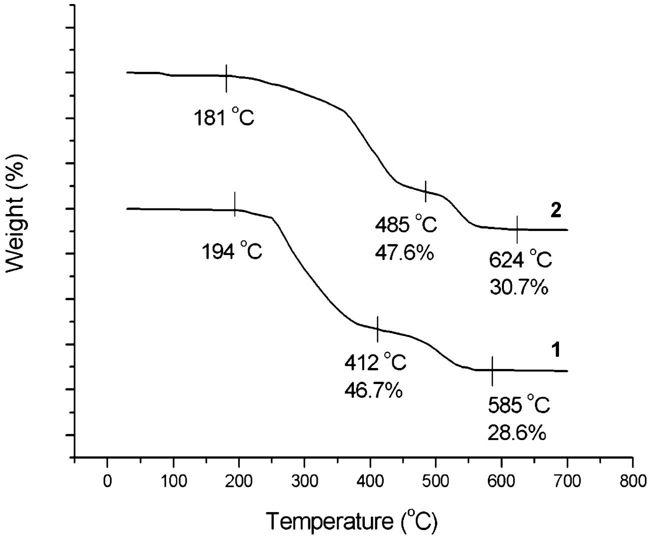

Figure 5. TG curves of **1** and **2**.

Table 4. Pyrolysis and TG Results for **1** and **2**

compd	temp range (°C) in TG	residue wt obsd (calcd) (%) in TG	residue wt in pyrolysis (%)	product of decomposition
1	194−412	46.7 (46.2)	28.9[a]	“[$MgIn_2S_3$(SC{O}Ph)$_2$]”
	412−585	28.6 (28.3)		$MgIn_2S_4$ (01-070-2893)
2	78−99	1.20 (1.30)	30.6[a]	anhydrous **2**
	181−485	47.6 (47.5)		“[$CaIn_2S_3$(SC{O}Ph)$_2$]”
	485−624	29.9 (28.8)		$CaIn_2S_4$ (00-31-0272)

[a] **1** and **2** were heated at 600 °C under 0.5 Torr of pressure for 6 h.

coordination sphere were formed. This is not surprising considering the hydrophilic nature and hydration energy associated with Ca^{II} ions.

Structure of 1. The neutral molecule consists of two tetrahedral [In(SC{O}Ph)$_4$]$^-$ anions in which each In^{III} center has four thiobenzoate anions bonded through the S atoms, as shown in Figure 1. These tetrahedral anions act as a metalloligand to sandwich a Mg^{II} metal ion. Each [In(SC{O}Ph)$_4$]$^-$ anion chelates a Mg^{II} ion through three carbonyl O atoms. In other words, each “In(SC{O}Ph)$_3$Mg” cage is comprised of three fused eight-membered rings. Thus, the coordination geometry around the Mg^{II} metal atom is distorted octahedral with an O_6 donor set. The In−S distances in **1** range from 2.453(2) to 2.512(2) Å, which are comparable to the In−S distances observed in the compound (Et_3NH)[In(SC{O}Ph)$_4$].[8a] The Mg−O distances are in the range from 2.006(4) to 2.060(4) Å. Large variations in the angles around the In^{III} [88.75(5)−124.23(8)°] and Mg^{II} [85.6(2)−176.9(2)°] metal ions are indicative of distortion from the ideal tetrahedral and octahedral geometries, respectively. A noncrystallographic center of inversion is present at the Mg^{II} atom.

Structures of 2a and 2b. As displayed in Figure 2, the molecular structure of **2a** also contains two tetrahedral [In(SC{O}Ph)$_4$]$^-$ anions chelating the Ca^{II} ion through five carbonyl O atoms. The coordination geometry at the Ca^{II} metal atom is distorted octahedral with an O_6 donor set, with

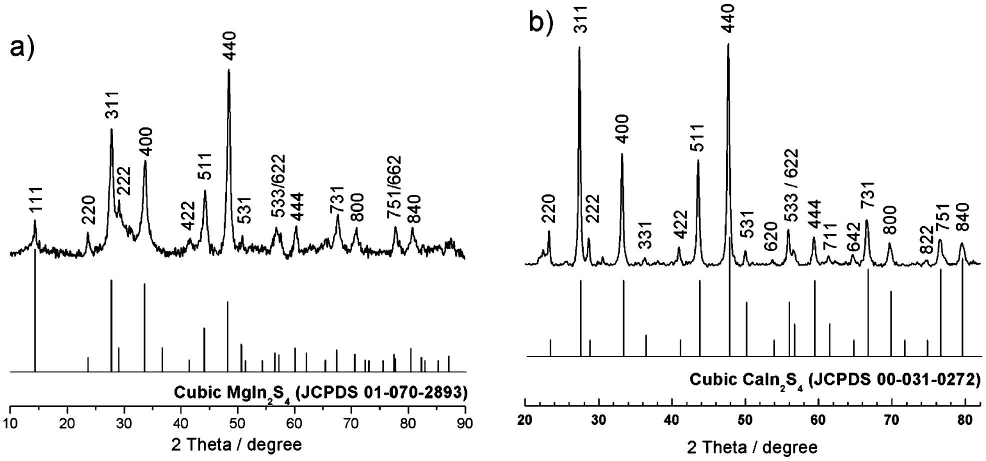

Figure 6. Powder X-ray diffraction patterns of the decomposed products of **1** (a) and **2** (b).

the sixth position occupied by an aqua ligand. The In$-$S distances in **2a** are in the range 2.441 (6)$-$2.514(4) Å and the Ca$-$O distances in the range 2.28(1)$-$2.32(1) Å. In^{III} and Ca^{II} metal centers in **2a** are also highly distorted from tetrahedral and octahedral geometries as inferred from a wide range of angles (Table 2).

The structure of **2b** shown in Figure 3 is very similar to that of **2a** but with a crystallographic 2-fold symmetry at Ca1. However, only two carbonyl O atoms from each [In(SC{O}Ph)$_4$]$^-$ anion are bonded to the Ca^{II} ion. The remaining two cis corners of the pseudo-octahedral geometry at Ca^{II} are occupied by two aqua ligands. The crystal has two lattice water molecules per formula unit.

The cis geometry at the Ca^{II} center helps the molecule remain packed to form a channel. All of the carbonyl O atoms and aqua ligands provide a hydrophilic environment for the channel in which the lattice water molecules have been trapped. Two symmetry-independent lattice water molecules sitting in a 2-fold crystallographic special position are alternatively bonded to the aqua ligands to generate a H-bonded water chain in the lattice, which propagates in the *c* direction, as shown in Figure 4. Selected H-bonding parameters are tabulated in Table 3. It may be noted that the lattice water molecules are further H-bonded to a carbonyl oxygen, O4, and a sulfur atom, S2, thereby stabilizing the structure.

Thermogravimetry and Pyrolysis. Metal chalcogenide compounds with composition II$-$III$_2$$-VI_4$ (where II = divalent metal, III = trivalent metal, VI = chalcogen) are the potential materials for optoelectronics applications.[18] Compounds **1** and **2** described here have the correct ratio of metals to serve as precursors for MIn$_2$S$_4$ compounds; hence, the thermal decompositions of **1** and **2** have been investigated using TG and are presented in Figure 5, and the results are summarized in Table 4. TG curves show that the inception of weight loss occurs at 194 and 181 °C for **1** and **2**, respectively. They decompose in two distinct steps in the temperature regions of 194$-$585 and 181$-$620 °C, respectively, and the final residues are expected to be MIn$_2$S$_4$. Hampden-Smith et al. have shown that metal thiocarboxylates can undergo a thiocarboxylic anhydride elimination reaction to form "MS".[6b]

The weight losses observed in the TG experiments agree well with the calculated values for the formation of the proposed intermediate "[MIn$_2$S$_3$(SC{O}Ph)$_2$]" and the loss of three S(C{O}Ph)$_2$ molecules (Table 4). The observed residual weight matched well with the calculated residual weight of MgIn$_2$S$_4$ but slightly higher for CaIn$_2$S$_4$ in both TG and pyrolysis experiments. The diffraction peaks shown in the X-ray diffraction patterns of the residues shown in Figure 6 can be assigned to the cubic-phase MgIn$_2$S$_4$ (JCPDS 01-070-2893) and the cubic-phase CaIn$_2$S$_4$ (JCPDS 00-31-0272) reported in the literature.[19] The mismatching of the intensity and poor agreement in the region $2\theta < 50°$ may be due to a combination of both the less crystalline nature of the compound and/or the preferred orientations of the crystallites. The single-source precursor method appears to be an alternative but attractive route to preparing MIn$_2$S$_4$ compounds, and the traditional synthetic method normally requires very high temperatures (<900 °C).[20]

Conclusions

We have shown that [In(SC{O}Ph)$_4$]$^-$ can be used as a metalloligand to bind to Mg^{II} and Ca^{II} ions and isolated **1** and **2**, which are molecular compounds unlike the alkali-metal derivatives of [In(SC{O}Ph)$_4$]$^-$.[4] In solution, [Ca{In(SC{O}Ph)$_4$}$_2$] can easily be hydrated because of the nature of the Ca^{II} ions, and two different hydrated crystalline forms were isolated. Of these, **2b** has an interesting channel created by [Ca{In(SC{O}Ph)$_4$}$_2$], trapping a single-stranded H-bonded water chain in the lattice. Thermal decomposition of these compounds led to the formation of MIn$_2$S$_4$ and was confirmed by the power X-ray diffraction patterns of the residues. On the basis of our investigations, **1** and **2** are useful precursors to the MIn$_2$S$_4$ materials. Further use of these

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precursors to make nanoparticles and thin films is under investigation.

Acknowledgment. We acknowledge the financial support of the National University of Singapore (Grant R143-000-283-112).

Supporting Information Available: Crystallographic data in CIF format and ORTEP diagrams of **1**, **2a**, and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060993N