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Mild Solvothermal Syntheses of Thioargentates A–Ag–S (A = K, Rb, Cs) and A–Ag–Ge–S (A = Na, Rb): Crucial Role of Excess Sulfur

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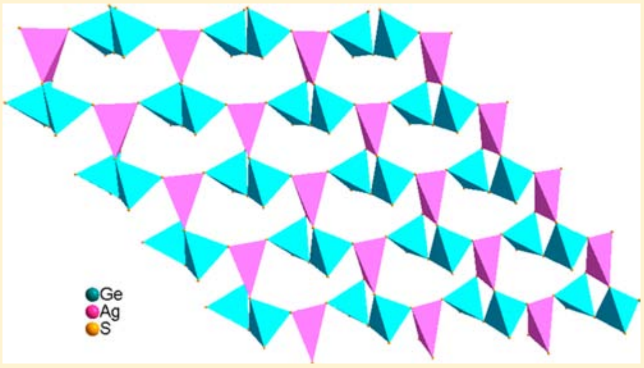
S *Supporting Information*

ABSTRACT: A series sulfides of A–Ag–S (**1**–**3**; A = K, Rb, Cs), $Na_5AgGe_2S_7$ (**4**), and $Rb_2Ag_2GeS_4$ (**5**) have been prepared solvothermally in the presence of excess sulfur. Among these compounds, **4** is a new compound that has a novel layered structure; the others were obtained under mild conditions. The results showed that excess sulfur could increase the solubility of silver sulfide and lower the synthetic temperature effectively. The mineralizer effect of excess sulfur is discussed in detail.



INTRODUCTION

Since Bedard and co-workers' patent for original microporous sulfides in 1989,[1] microporous chalcogenides have attracted much attention because of their intriguing structures[2−5] and potential applications such as fast-ion conductors,[6] selective ion exchangers,[7] and efficient visible-light photocatalysts.[8−10]

Recently, increasing interest in this field is the incorporation of transition-metal ions into main-group chalcogenides to enrich the structural diversity and properties of the chalcogenides. In view of the vast number of molecular building blocks for main-group chalcogenides[11,12] and the coordination chemistry of a variety of transition metals (Mn, Fe, Cu, Zn, Ag, Hg, etc.),[13] the number of known quaternary phases formed by main-group and transition metals is surprisingly small in comparison with the numerous ternary compounds. This fact implies that the syntheses and characterization of quaternary compounds is still in its infancy; in spite of that, the progress in this field has been encouraging.[14,15]

Common techniques employed to synthesize metal chalcogenides at intermediate temperatures (100−600 °C) include flux and solvothermal methods.[14−18] Under these relatively mild conditions, molecular building blocks can self-organize to various fascinating frameworks whose structures can be influenced by the choice of suitable structure-directing agents such as alkali metals or alkylammonium cations. In addition, mild temperatures make metastable chalcogenides with unusual functionality available. Although a number of new compounds remain to be discovered at high temperatures, the thermodynamically stable phases often cannot be avoided under these synthetic conditions. Therefore, mild syntheses are promising ways to access new materials of chalcogenides.

A challenging problem in mild syntheses of quaternary chalcogenides is the very small solubility of transition-metal chalcogenides, which often leads to a failure to incorporate transition-metal ions into main-group chalcogenides and therefore greatly limits the number of quaternary chalcogenides. A variety of synthetic strategies have been developed to improve the solubility of transition-metal chalcogenides, some of which involve increasing the synthetic temperature. For example, carrying out synthetic reactions in molten alkali-metal (poly)chalcogenides or utilizing a supercritical solvothermal method.[18−23]

Mild hydro/solvothermal reactions (120−200 °C) evidently provide the preferred route to quaternary chalcogenides if a suitable mineralizer could be chosen.[24] Our previous research has shown that both thiol and thiophenol are effective mineralizers for the synthesis of quaternary sulfides because of their ability to form soluble complexes with transition-metal cations such as Ag^+ and Hg^{2+}.[25−29]

From the viewpoint of the solubility equilibrium, the solubility of transition-metal chalcogenides can be increased alternatively by decreasing the concentration of chalcogenide anions E^{2-} (E = S, Se, Te). This can be realized by the reaction between elemental chalcogen E and chalcogenide anion E^{2-} to form polychalcogenide species E_x^{2-} in solution.[14,30] This means that sulfur powder can decrease the concentration of S^{2-} by the generation of polysulfide ions S_x^{2-}, consequently shifting the equilibrium to increase the solubility of transition-metal sulfides.

Sulfur powder is commonly used in the solvothermal syntheses of metal sulfides, and the typical molar composition of S/M (M standing for metal) used for the syntheses is 2−3.[1−10,20−23,25−29,31] In these cases, the effect of sulfur powder

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on the solubility of metal sulfides might not be evident because of its slight excess; namely, the effect of a large excess of sulfur powder has not been explored yet. In order to test the mineralizer effect of a large excess of sulfur, we chose silver sulfide as the research object because of its very small solubility.

Here we report the solvothermal syntheses of a series of sulfides A–Ag–S (**1**–**3**; A = K, Rb, Cs) and A–Ag–Ge–S (**4** and **5**; A = Na, Rb) in the presence of excess sulfur. Compared with the previous reports, AAg_5S_3 (**1** and **2**; A = K, Rb), $CsAg_7S_4$ (**3**), and $Rb_2Ag_2GeS_4$ (**5**) were obtained under more mild conditions, and a new layered compound, $Na_5AgGe_2S_7$ (**4**), was also synthesized under a similar synthetic condition.

■ EXPERIMENTAL SECTION

Materials and Physical Measurements. All reagents were purchased from commercial sources and used without further purification. Energy-dispersive spectroscopy (EDS) analyses were performed using a Quanta 450 instrument on handpicked crystals. Powder X-ray diffraction (XRD) was measured using a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The data were collected at room temperature with a step size of 0.02° and an X-ray tube power of 3 kW.

Syntheses. These compounds were synthesized by similar procedures. The mixture of reactants was placed in a Pyrex glass tube (12 cm length and 7 mm i.d.). The tube was sealed with ca. 10% filling under an air atmosphere, placed in a stainless-steel autoclave, and heated at 160 °C (150 °C for **3** and 170 °C for **4** and **5**) for 5 days. Cooled naturally to ambient temperature, final products shaped as dark-red blocks (black for **3**, colorless for **4**, and pale yellow for **5**) were obtained after washing several times with ethanol and deionized water (note that **4** is water-sensitive), respectively, and dried at room temperature.

KAg_5S_3 (**1**) was synthesized using 32 mg of sulfur powder (1.00 mmol), 20 mg of K_2CO_3 (0.14 mmol), 12 mg of $AgNO_3$ (0.07 mmol), and about 0.5 mL of 1,2-diaminopropane (1,2-DAP).

$RbAg_5S_3$ (**2**) was prepared using 40 mg of sulfur powder (1.25 mmol), 12 mg of Rb_2CO_3 (0.05 mmol), 12 mg of $AgNO_3$ (0.07 mmol), and about 0.5 mL of 1,2-DAP/pyridine ($V_{1,2\text{-DAP}}/V_{\text{pyridine}}$ = 1).

$CsAg_7S_4$ (**3**) was prepared using 25 mg of sulfur powder (0.78 mmol), 10 mg of Cs_2CO_3 (0.03 mmol), 12 mg of $AgNO_3$ (0.07 mmol), and about 0.5 mL of 1,2-DAP/pyridine ($V_{1,2\text{-DAP}}/V_{\text{pyridine}}$ = 1). The results of EDS analyses for **1**–**3** are summarized in Table 1.

Table 1. EDS Analysis Results

compound	A (K, Rb, Cs)	Ag	S	approximation
1	9.15	55.18	35.67	1:5:3
2	9.63	55.92	34.45	1:5:3
3	8.19	57.63	34.18	1:7:4

$Na_5AgGe_2S_7$ (**4**) was prepared using 2 mg of GeO_2 (0.02 mmol), 5 mg of $AgNO_3$ (0.03 mmol), 14 mg of sulfur (0.44 mmol), 10 mg of CH_3COONa (0.12 mmol), and about 0.4 mL of 1,2-DAP.

$Rb_2Ag_2GeS_4$ (**5**) was synthesized using 1 mg of germanium powder (0.01 mmol), 2 mg of $AgNO_3$ (0.01 mmol), 6 mg of sulfur (0.19 mmol), 5 mg of RbCl (0.04 mmol), and about 0.4 mL of triethylenetetramine (TETA).

Actually, compounds **1**–**3** can be obtained at a temperature of 140 °C. The above-mentioned syntheses for **1**–**3** were directed to produce single crystals suitable for X-ray structural analysis.

Crystallographic Studies. Crystallographic data collections were performed on a Bruker Smart APEX II diffractometer equipped with graphite-monochromitized Mo Kα radiation (λ = 0.71073 Å) at room temperature. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using *SHELX97*.[32] All non-H atomic positions were located in Fourier maps and refined anisotropically based on F^2 using *SHELX97*.[33] Experimental details for structure determination are presented in Table 2. The selected bond distances and bond angles of the five compounds are presented in Tables S1–S5 (Supporting Information).

■ RESULTS

Although **1**,[34] **2**,[21,34] and **3**[21] were first synthesized by Kolis et al. in supercritical ethylenediamine (en) at a temperature above 300 °C, we successfully obtained **1**–**3** at a mild temperature of 140 °C in the presence of a large excess of sulfur.

We previously prepared **5** using thiol as a mineralizer.[35] The crystal can also be isolated by employing excess sulfur instead of the thiol. The thiol is not stable enough because the –SH group easily falls off at a temperature higher than 120 °C; therefore, it cannot work well at high temperature. Thiophenol is more stable and a valid mineralizer for the syntheses of **1**–**3**. However, the vital shortfall of thiophenol is its high toxicity.

4 is a novel layered compound with sheets containing Ag atoms coordinated in a distorted tetrahedral fashion [S–Ag–S angles range from 80.31(5) to 137.49(4)°] and dimeric clusters $[Ge_2S_7]^{6-}$ constructed from two corner-sharing GeS_4, with S–Ge distances ranging from 2.1893(13) to 2.2472(12) Å, to form a fused 14-membered ring (see Figure 1). The charge-balancing Na^+ cations lie between the layers.

Krebs has reviewed thoroughly the chemistry of isolated clusters of thio- or selenogermanates.[12] Condensation of tetrahedral $[GeE_4]^{4-}$ in polar solvents generally leads to the formation of respectively corner- and edge-bridged dimeric $[Ge_2E_7]^{6-}$ and $[Ge_2E_6]^{4-}$ anions or adamantane-like $[Ge_4E_{10}]^{4-}$ species, all of which have been structurally characterized in the presence of alkali-metal counterions. The generic structures of these anions are shown in Figure 2.

In view of the known germanium-containing quaternary chalcogenides, $[Ge_4E_{10}]^{10-}$ is the most common building block that is usually found to be linked by binders like M^{2+} (M = Fe, Co, Zn, Cd, Hg) or M^+/M_2^{2+} (M = Cu, Ag),[29,36−43] or partly substituted by tetrahedral transition metals to form extended open frameworks such as $K_4Ag_2Ge_3S_9\cdot H_2O$[44] and $[Et_4N]_4M_4S_{10}$ (M = Zn/Ge).[45] By contrast, relatively few examples have been reported for structures based on the dimeric $[Ge_2E_7]^{6-}$ moiety. In $[Mn(dien)_2]_2Ge_2Se_7$ (dien = diethylenetriamine) and $(enH_2)[\{Mn(en)_2(enH)\}_2(\mu\text{-en})]Ge_2Se_7$, $[Ge_2Se_7]^{6-}$ is the isolated dimeric cluster.[46] It has also been shown in $[\{Mn(cyclam)\}_2(\mu\text{-}Ge_2Se_7)]\cdot CH_3OH\cdot 1.5H_2O$ that the selenogermanate anion can bridge two $[(cyclam)Mn]^{2+}$ fragments in a spirotricyclic manner.[47] To the best of our knowledge, **4** is the first 2D sulfide in which the dimeric $[Ge_2S_7]^{6-}$ cluster forms part of the bonding network.

Through a comparison among **4**, $K_2Ag_2GeS_4$,[35] and **5**, we found that, with the increasing radius of the cation from Na^+ to Rb^+, there is a significant variation in the primary building blocks, namely, the $[GeS_4]^{4-}$ moiety takes the place of $[Ge_2S_7]^{6-}$. This change may be attributed to the structure-directing effect of alkali metals. The small alkali metal Na^+ promotes the formation of high-charge-density anionic clusters.

■ DISCUSSION

In the hydro/solvothermal synthesis, a mineralizer plays an important role. It speeds up crystallization through increasing the solubility of the reactants. Typical mineralizers are alkali-metal hydroxides, especially for the growth of amphoteric and acidic oxides such as silicates, germinates, etc. Additionally, salts of weak acids, e.g., Na_2CO_3, and alkali-metal chlorides as well as acids are applied.[24] For the solvothermal syntheses of sulfides,

Table 2. Crystal Data and Structure Refinement

compound	1	2	3	4	5
empirical formula	KAg_5S_3	$RbAg_5S_3$	$CsAg_7S_4$	$Na_3AgGe_2S_7$	$Rb_2Ag_2GeS_4$
fw/g mol^{-1}	674.66	309	1016.24	592.42	587.51
temperature/K	296	296	296	296	296
cryst syst	hexagonal	hexagonal	tetragonal	monoclinic	monoclinic
space group	$P\overline{6}2c$	$P\overline{6}2c$	$P4/n$	$C2/c$	$C2/c$
unit cell dimens					
a/Å	13.2208(12)	13.2960(9)	11.1002(13)	9.1456(18)	7.4774(3)
b/Å				10.2611(19)	22.1120(7)
c/Å	7.9479(14)	8.0060(11)	8.531(2)	14.863(3)	6.2963(2)
β/deg				104.315	115.664
γ/deg	120	120			
V/Å^3	1203.1(3)	1226(2)	1051.1(3)	1351.5(4)	938.33(6)
Z	6	6	4	4	4
calcd density/Mg m^{-3}	5.587	5.86	6.422	2.912	4.159
reflns collected/unique	5904/1031 [R(int) = 0.0287]	6518/1074 [R(int) = 0.0623]	5690/1221 [R(int) = 0.0306]	3700/1189 [R(int) = 0.0196]	2650/830 [R(int) = 0.0460]
GOF on F^2	1.333	1.062	1.075	1.136	0.887
final R indices [$I > 2\sigma(I)$]	R1 = 0.0336, wR2 = 0.0797	R1 = 0.0339, wR2 = 0.1113	R1 = 0.0308, wR2 = 0.0696	R1 = 0.0270, wR2 = 0.0751	R1 = 0.0375, wR2 = 0.1077

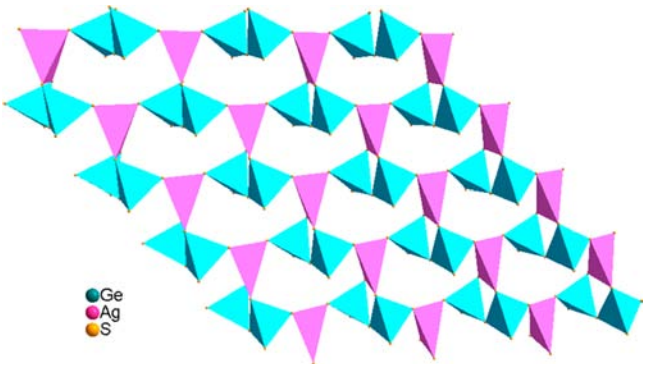

Figure 1. Top view of the 2D sheet structure of **4**. Na^+ cations are omitted for clarity.

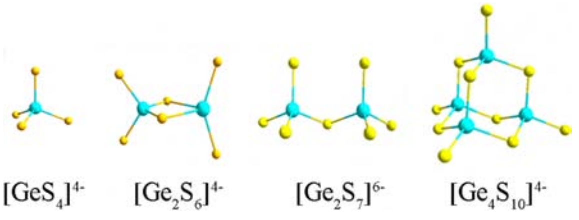

Figure 2. Generic structures of molecular anions that can serve as molecular building blocks.

especially group 14/15 element sulfides, alkali-metal sulfides are usually used as mineralizers because of their ability to produce various soluble thioanions.[48,49] In contrast, these tactics seldom work on solvothermal syntheses of transition-metal sulfides.

The above-mentioned research has shown that excess sulfur is a mineralizer for silver sulfide. According to the literature, elemental sulfur can react readily with the sulfide anion S^{2-} to form soluble polysulfide chains.[50,51]

$$(x - 1)S + S^{2-} \rightleftharpoons S_x^{\ 2-}$$

With an increase in the amount of sulfur in a solvothermal system, the condensation degree of polysulfide species will grow, meanwhile the concentration of the isolated sulfide anion S^{2-} will decrease gradually. In the presence of excess sulfur, the solubility equilibrium of silver sulfide will be driven to the right, benefiting dissolution of the sulfide under solvothermal conditions.

$$Ag_2S \rightleftharpoons 2Ag^+ + S^{2-}$$

Our experimental results showed that a certain amount of Cu_2S and Ag_2S can dissolve solvothermally in en to form clear solutions in the presence of excess sulfur. The molar ratio S/Cu of 7 is needed to dissolve 0.05 mmol of Cu_2S in 0.5 mL of en at 150 °C for 5 days, and the ratio S/Ag is larger than 20 to dissolve 0.05 mmol of Ag_2S in 0.5 mL of en. The amount of sulfur needed to dissolve silver sulfide is much more than that for the copper analogue under similar conditions. This is in agreement with their solubility data; namely, Ag_2S has a much smaller solubility than Cu_2S. This characteristic is also reflected in our previous work.[52−54]

We discussed the effect of excess sulfur on hydro/solvothermal syntheses only from the viewpoint of the reaction between S^{2-} and S to generate $S_x^{\ 2-}$. In fact, soluble complexes of transition metals with some polysulfide anions may be involved during the syntheses. The internal S atoms of the chain $S_x^{\ 2-}$ have near-zero formal charge; the negatively charged terminal S atoms are available for transition-metal ions such as Zn, Mn, Au, and Cu to form soluble complexes, for example, $[Zn(S_4)_2]^{2-}$, $[Mn(S_5)(S_6)]^{2-}$, $[AuS_9]^-$, and $[(S_6)Cu(\mu\text{-}S_8)Cu(S_6)]^{4-}$.[55−57]

From the above discussion, the function of excess sulfur in the solubility equilibrium of transition-metal sulfides may be dual, i.e., lowering the concentration of sulfide anion S^{2-} by the formation of $S_x^{\ 2-}$, on the one hand, and decreasing the concentration of the transition-metal cation by forming polysulfide complexes, on the other hand. Therefore, excess sulfur can be an effective mineralizer for syntheses of silver chalcogenides.

Because of the good solubility of M_2S (M = Ag, Cu) in the presence of excess sulfur, this method is suitable for synthesizing silver-rich sulfides solvothermally such as Ag_3AsS_3 and Ag_3SbS_3 under mild conditions. Although these phases had been prepared previously,[58,59] we were able to obtain both compounds at temperatures from 140 to 170 °C in various amine systems, e.g., en, 1,2-DAP, dien, and TETA.

During the syntheses of **4** and **5**, we found that the presence of thiogermanates also facilitates the dissolving of Ag_2S. Therefore, the amount of sulfur used can be decreased. The reason may be that main-group 14 binary sulfides are soluble in an alkaline sulfide solution to form thioanionic clusters with different condensation degrees because of the acidic nature. These anions can coordinate to Ag^+, increasing the solubility of silver sulfide.

The alkali-metal polychalcogenide flux technique is a good method to synthesize quaternary chalcogenides.[18,60,61] The reaction nature of our method is the same as that of the flux method in some aspects; e.g., in both methods, the polysulfide species are not only mineralizers but also reactants of the synthetic reactions. The advantage of our method is the mild conditions. Therefore, organic cation-templated chalcogenides can be synthesized using this method. Organic templates are very important in the syntheses of many chalcogenides; for instance, $[R_4N]^+$ (R = Me, Et, nPr) or $[enH_2]^{2+}$ are of importance in the syntheses of microporous chalcogenide materials to regulate the size and shape of the channels. In addition, our method is more convenient to operate. On the basis of literature precedents, elemental sulfur can be activated by nucleophilic attack by a base.[50] Hence, the sulfide ions S^{2-} needed for the formation of polysulfide intermediates S_x^{2-} and the final products can be generated in situ using an organic amine or alkaline aqueous solution as the solvent. Moreover, the syntheses also can be carried out in aqueous systems. The presence of large organic cations such as $[(Me)_4N]^+$ and $[(Et)_4N]^+$ makes the hydrophobic polysulfides more soluble. We successfully obtained several open-framework indium chalcogenides built from T5 clusters with different patterns in aqueous systems.[62]

The careful choice of both the solvent and cation is necessary for the preparation of pure phases. The polarity of the solvent is a significant effect because the polarity of the polychalcogenide E_x^{2-} chains decreases with the length. In other words, the solubility of long chains E_x^{2-} will be small in a polar solvent such as water, especially when small alkali cations exist in the reaction system.[14,30] Therefore, various organic amines are more preferred than water or alcohol for the syntheses of metal chalcogenides.

The influence of the cation is reflected not only in the stabilization of the polychalcogenide ions $E_x{}^{2-}$ but also in the formation of the products. To some extent, the size of the cation determines whether it can enter the product or not. For example, large cations such as R_4N^+ (R = Me, Et, Pr^n, Bu^n) or Ph_4P^+ are generally required to form thioanions of higher nuclearity.[14,30,55−57,60,63] We found that Ag_3AsS_3 is the only product when $[(Me)_4N]^+$ exists in the solvothermal system of $Ag_2S-As_2S_3$ amines. In this case, the polysulfides only play the role of a mineralizer. However, when small cations such as K^+, Rb^+, and Cs^+ exist in the reaction system, MAg_2AsS_3 (M = K, Rb, Cs)[30,64] can be obtained. The alkali polysulfides play the roles of both a mineralizer and a reactant. This means that ternary and quaternary sulfides could be accessed through the appropriate choice of cations.

Generally speaking, the larger the amount of sulfur, the less the concentration of S^{2-} is. This condition will facilitate dissolution of silver sulfide. However, it should be noted that too much sulfur will increase the viscosity of the solvent and retard crystallization of the products. Long polysulfide chains are difficult to dissolve in the polar solvent because of their poor polarity. A moderate increase in the temperature can improve the situation to some extent.

Se is chemically similar to S, although less reactive, and has a larger ability to form chains than S does. The chemistry of polyselenide Se_x^{2-} and their transition-metal complexes are well established since 1990.[60,61] Representative examples are provided by the bridging Se_5^{2-} and Se_6^{2-} ligands in $KAuSe_5$, K_3AuSe_{13}, and $[Mn(Se_6)(cyclam)]_2$ (cyclam = tetraazacyclotetradecane) and the chelating ligand Se_4^{2-} in $[Mn(Se_4)(terpy)]$ (terpy = 2,2′;6,2″-terpyridine).[65−67] On the basis of the similarity between S and Se, we extended the present method to the synthesis of selenides and successfully synthesized M−Ag−Se (M = K, Rb, Cs) compounds in the en system at 150 °C. Powder XRD research showed that the resulting compounds were pure phases. Further studies were not conducted because of their highly toxic nature. Compared with the corresponding sulfides, these syntheses were relatively easier, and the Se/Ag ratio (usually 6) is much smaller than the S/Ag ratio for the sulfides.

Preliminary research showed that the method could work on divalent transition-metal sulfides MS (M = Zn, Mn, Ni, Co), whose solubility products ranged from 10^{-10} to 10^{-30}.[68] The equilibrium concentration of the sulfide anion S^{2-} should be much larger than those for M_2S (M = Ag, Cu) when the concentrations of the metal cations are the same. Therefore, the present method is more convenient and safe compared with the synthetic route in which thiol or thiophenol was used as a mineralizer.

■ CONCLUSION

The mild solvothermal syntheses of a series of sulfides A−Ag−S (**1**−**3**; A = K, Rb, Cs) and A−Ag−Ge−S (**4** and **5**; A = Na, Rb) were carried out in the presence of excess sulfur. It was found that excess sulfur is an effective mineralizer for the syntheses, reducing the synthetic temperatures effectively. Compared with the thiol and thiophenol, elemental sulfur is easy to use, safe, and environmentally friendly.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Results of EDS for compounds **1**−**3**, powder XRD patterns for compounds **1**−**3** and **5**, selected bonds and angles, and crystallographic information files in CIF format for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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