General Synthesis of Metalloid Polysulfide Complexes from the Elements: Structures of $Sb_2S_{15}^{2-}$ and $InS_8(N\text{-}MeIm)^-$

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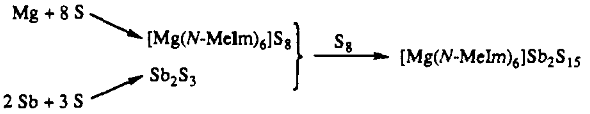
In previous reports we have described the use of strong donor solvents such as *N*-methylimidazole (*N*-MeIm) to promote the reaction of certain first-row transition metals with sulfur. These L–M–X reactions afford the charge neutral complexes $Cu_4(S_5)_2(N\text{-}MeIm)_4$ and $ZnS_6(N\text{-}MeIm)_2$ and the octasulfide salts $[M(N\text{-}MeIm)_6]S_8$ (M = Mn, Fe, Ni).[1] Sen has employed this methodology to prepare $[Cd(N\text{-}MeIm)_6][Cd(S_6)_2]$.[2] However, we were surprised to find that metals that form particularly strong M–S bonds, as indicated by the low-solubility products of their binary sulfides (e.g., Hg, Ag, Sn), do not dissolve in *N*-MeIm solutions of sulfur. As described below, this difficulty has been overcome, leading to a new protocol for solution syntheses of polysulfide complexes from elemental precursors.

Illustrative of our methodology is the time-honored Hg + S_8 reaction. Mercury reacts with an *N*-MeIm solution of S_8 to give a dark precipitate of HgS_x. Addition of 1 equiv of Mg and warming (80 °C for 50 h) results in complete conversion of the metals, precipitating green microcrystals of $[Mg(N\text{-}MeIm)_6][Hg(S_4)_2]\cdot N\text{-}MeIm$. Starting with 0.47 g of Hg, 0.6 g of S_8, 0.057 g of Mg, and 10 mL of *N*-MeIm, one obtains 2.15 g (87%) of the polythiomercurate salt.[3] This route to polysulfide complexes from the elements has some generality (Scheme I).[4]

The versatility of the new method allows one to systematically explore the polysulfido complexes of a range of metalloids. In this way we have prepared the first antimony polysulfide from the reaction of a stirred suspension (80 °C) of 0.065 g of Mg, 0.319 g of Sb powder (200 mesh), 1.245 g of sulfur, and 13 mL of *N*-MeIm. Over the course of 48 h, we observed the disappearance of the metal powder and the formation of a yellow-orange precipitate. The orange powder of $[Mg(N\text{-}MeIm)_6]Sb_2S_x$ ($x \sim 15$) was filtered and washed with *N*-MeIm (10 mL) and Et_2O (45 mL) for a yield of 1.4 g (88% yield).[5] A suspension of 0.716 g of this orange salt in 10 mL of DMF dissolved upon addition of 0.49 g of PPh_4Br. The red-orange product was precipitated with 20 mL of toluene, washed with Et_2O, and recrystallized from DMF–toluene. The IR spectra of the PPh_4^+ and $[Mg(N\text{-}MeIm)_6]^{2+}$ salts of $Sb_2S_{15}^{2-}$ are identical in the range of 500–400 cm^{-1} where we observed ν_{SS} bands at 487 and 461 cm^{-1}. The visible spectrum of $(PPh_4)_2Sb_2S_{15}\cdot PhMe$ is dominated by an intense band at 322 nm. The anion's resilience to cation exchange and its *nondissociation* into polysulfido anions (cf. S_3^-, λ_{max} = 608 nm) suggest that $Sb_2S_{15}^{2-}$ remains intact in solution.

Crystallographic analysis of the PPh_4^+ salt shows that the dianion $Sb_2S_{15}^{2-}$ adopts a beautiful tricyclic structure (Figure 1).[6] It cocrystallizes with $Sb_2S_{16}^{2-}$ such that SbS_6 rings replace SbS_5 with 27% occupancy. The SbS_5 rings adopt a chair conformation, while the SbS_6 rings resemble cyclo-S_7. The antimony centers, which are crystallographically equivalent via a 2-fold axis, are four coordinate. In contrast, Siewert and Müller's S_7AsS^- features a tricoordinate As center.[7] The trend for higher coordination numbers as one descends a column continues also for the bismuth polysulfide $Bi_2S_{34}^{4-}$, which features five-coordinate Bi.[8] The Sb centers adopt a distorted SF_4-like geometry where the widest S–Sb–S angle (S2–Sb–S4) is 166.5° and the smallest (S4–Sb–S1) is 78°. The other four angles lie between 87.0 and 90.5°. On the basis of the S–Sb–S angles and ring conformation, the nonbonding electron pairs on Sb project toward opposite sides of the central 1,3-Sb_2S_5 ring.

The Mg-assisted dissolution of thiophilic metals is thought to occur in three distinct stages (eq 1). First, Mg reduces the sulfur, leading to the $[Mg(N\text{-}MeIm)_6]^{2+}$ salt of S_8^{2-}. The octasulfide ion exists in equilibrium with S_8, S_6^{2-}, S_3^-, and probably other species.[1c] Second, an independent process, is the sulfiding of the thiophilic metal. Third is the step involving attack of the polysulfido anions on the polymeric metal sulfide. Consistent with this scenario is the synthesis of $Sb_2S_{15+x}^{2-}$ salts via the dissolution (48 h, 80 °C) of 0.320 g of the mineral Sb_2S_3 (Cerac) in a preformed *N*-MeIm solution of sulfur and $[Mg(N\text{-}MeIm)_6]S_8$ (0.0239 g of Mg, 0.420 g of S_8) in 12 mL of *N*-MeIm for a yield of 0.9 g of $[Mg(N\text{-}MeIm)_6]Sb_2S_{15+x}$ (77%).



(1)

Our method is related to the use of thioanions as mineralizers in the syntheses of metal sulfides (and analogous processes involving selenides).[9,10] Of particular relevance to the present work are the polymeric thioantimonates $Sb_3S_5^-$, $Sb_4S_7^{2-}$, and $Sb_{10}S_{18}^{6-}$.[10] The present method differs from classical hydrothermal and related flux routes in that the *N*-MeIm is more directly

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(1) (a) Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 4043. (b) Dev, S.; Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 4044. (c) Dev, S.; Ramli, E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 2514. (d) Rauchfuss, T. B.; Dev, S.; Wilson, S. R. *Inorg. Chem.* **1992**, *31*, 153. (e) Krautscheid, U.; Dev, S.; Krautscheid, H.; Paul, P. P.; Rauchfuss, T. B.; Wilson, S. R. *Z. Naturforsch.* In press.

(2) Wozniak, M. E.; Sen, A.; Rheingold, A. L. *Chem. Mater.* **1992**, *4*, 753.

(3) Anal. Calcd for $C_{28}H_{42}N_{14}HgMgS_8$: C, 31.8; H, 4.02; N, 18.5; Hg, 19.0; Mg, 2.30. Found: C, 31.3; H, 4.07; N, 18.0; Hg, 18.9; Mg, 2.13. The corresponding $Fe(N\text{-}MeIm)_6^{2+}$ salt was also prepared by using Fe powder in place of Mg.

(4) Salts of known polysulfide anions were characterized by elemental analysis and IR spectroscopy. Leading references are as follows $Ag_2S_{12}^{2-}$: Müller, A.; Krickemeyer, E.; Zimmermann, M.; Römer, M.; Bögge, H.; Penk, M.; Schmitz, K. *Inorg. Chim. Acta.* **1984**, *90*, L69. $Au_2S_8^{2-}$: Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Schmitz, K. *Inorg. Chim. Acta.* **1984**, *85*, L39. HgS_8^{2-}: Bailey, T. D.; Herath Banda, R. M.; Craig, D. C.; Dance, I. G.; Ma, I. N. L.; Scudder, M. L. *Inorg. Chem.* **1991**, *30*, 187. SnS_{14}^{2-}: Müller, A.; Schimanski, J.; Römer, M.; Bögge, H.; Baumann, F.-W.; Eltzner, W.; Krickemeyer, E.; Billerbeck, U. *Chimia* **1985**, *39*, 25. CdS_{12}^{2-}: Herath Banda, R. M.; Dance, I. G.; Bailey, T. D.; Craig, D. C.; Scudder, M. L. *Inorg. Chem.* **1989**, *28*, 1862. Reviews: (a) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742. (b) Müller, A.; Diemann, E. *Adv. Inorg. Radiochem.* **1987**, *31*, 89. (c) Kanatzidis, M. *Comments Inorg. Chem.* **1990**, *10*, 161. (d) Ansari, M.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223.

(5) Anal. Calcd for $C_{24}H_{36}N_{12}MgSb_2S_{15.54}$: C, 22.90; H, 2.88; N, 13.35; Mg, 1.93; Sb, 19.34. Found: C, 22.12; H, 2.69; N, 12.28; Mg, 1.93; Sb, 19.86. Anal. Calcd for $C_{55}H_{48}P_2Sb_2S_{15.54}$: C, 43.38; H, 3.17. Found: C, 43.28; H, 3.20. Elemental analyses must be interpreted with caution in view of the well-known nonstoichiometry of polysulfide complexes. The conductivity of a DMF solution of $(PPh_4)_2Sb_2S_{15}$ is 98 Ω^{-1} cm^2 mol^{-1}, in the range for other 2:1 electrolytes.

(6) $C_{48}H_{40}P_2Sb_2S_{15}\cdot C_7H_8$ crystallizes in the monoclinic space group *I*2/*a* (No. 15); a = 19.689(5), b = 13.758(4), and c = 22.891(7) Å; $\alpha = \gamma = 90°$, $\beta = 95.31°$. Of 4129 reflections collected (−35 °C, Mo Kα: $2.0 < 2\theta < 45.4°$, ω/θ mode), 2419 ($I > 2.58\sigma(I)$) were refined to R = 0.057, R_w = 0.061. $C_{32}H_{42}N_{16}In_2MgS_{16}$ crystallizes in the trigonal space group *R*3 (No. 148), $a = b$ = 23.962(5) and c = 25.873(6) Å, $\alpha = \beta = 90°$, $\gamma = 120°$. Of 3735 reflections collected (−75 °C, Mo Kα; $2.0 < 2\theta < 45°$, ω/θ scan mode) 2844 ($I > 2.58\sigma(I)$) were refined to R = 0.041, R_w = 0.044.

(7) Siewert, B.; Müller, U. *Z. Anorg. Allg. Chem.* **1991**, *595*, 211.

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(10) Sheldrick, W. S.; Haüsler, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 105. Parise, J. B. *Science* **1991**, *251*, 293. Parise, J. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1553. Parise, J. B.; Ko, Y. *Chem. Mater.* **1992**, *4*, 1446.

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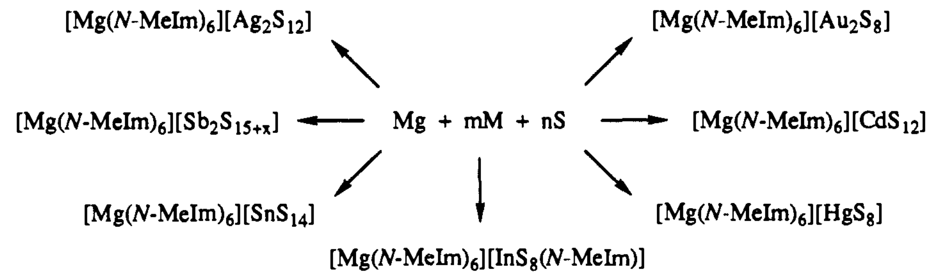
Scheme I



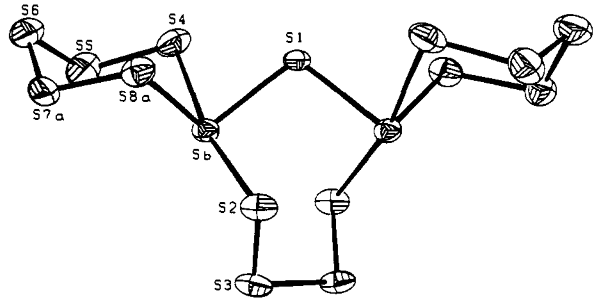


Figure 1. ORTEP plot of the anion $Sb_2S_{15}^{2-}$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å): Sb–S1, 2.421(3); Sb–S2, 2.667(4); Sb–S4, 2.648(4); Sb–S8a, 2.550(6).

involved in the mobilization of the metals (and metalloids) as a consequence of its considerable coordinating power.[11] The important role of the *N*-MeIm in the solvation of ***both*** the cations and the anions is illustrated by the synthesis and structure of $[Mg(N\text{-}MeIm)_6]\{In(S_4)_2(N\text{-}MeIm)\}_2$.[6,12] Large yellow crystals of this very air-sensitive salt were obtained by reaction of 0.027 g of Mg, 0.252 g of In, and 0.710 g of sulfur (a 1:2:16 atomic ratio) in 17 mL of *N*-MeIm at 90 °C. After 48 h the reaction solution was filtered and diluted with 40 mL of Et_2O. The precipitate was extracted into 25 mL of THF and crystallized by layering with toluene to give 0.45 g (29%). The coordination geometry for In is distorted trigonal bipyramidal (tbp) with the *N*-MeIm in an equatorial site (Figure 2). The axis of the tbp is defined by S5–In–S1 (176.9°). The related anion $[In(S_4)(S_6)Br]^{2-}$ has been prepared previously by metathetical routes.[13] In the latter, the S_6^{2-} chelates equatorial positions (S–In–S = 115.7°), while the S_4^{2-} spans both axial and equatorial sites (91.0°). The chelate bite angle determines the length of the polysulfide chain.

The *N*-MeIm/M + Mg/S_8 method also has been employed in the synthesis of a lead polysulfide $[Mg(N\text{-}MeIm)_6][PbS_x]$ ($12 < x \leq 14$). Although problems with disorder have thus far prevented a detailed evaluation of its structure, it appears that this is a spirocyclic species corresponding to $Pb(S_x)_2^{2-}$, where x = 6 or 7. Thallium dissolves in the presence of Mg and S_8, but we have not yet crystallized this product.

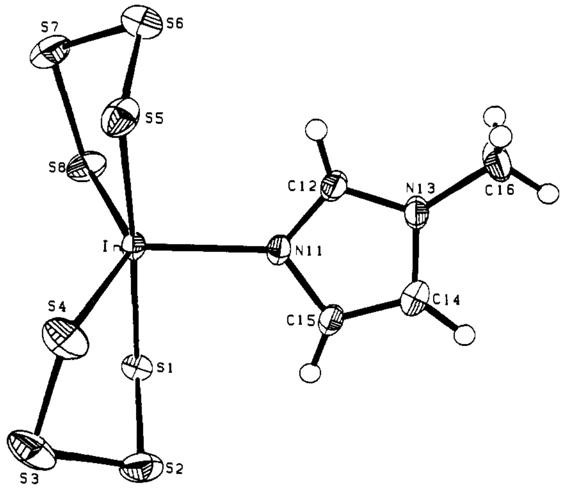


Figure 2. ORTEP plot of the anion $[InS_8(N\text{-}MeIm)]$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å): In–S1, 2.593(2); In–S4, 2.490(2); In–S5, 2.576(2); In–S8, 2.503(2); In–N11, 2.222(5).

In summary, the *N*-MeIm/(M + M′)/S_8 method allows one to prepare a range of polysulfide complexes from the simplest reagents under mild conditions.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, atomic coordinates, and thermal parameters for $[Sb_2S_{15}][(C_6H_5)_4P]_2{\cdot}C_7H_8$ and $[InS_8(C_4H_6N_2)]_2[Mg(C_4H_6N_2)_6]$ (24 pages); listing of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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[11] Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471.

[12] Anal. Calcd for $C_{32}H_{48}N_{16}MgIn_2S_{16}$: C, 26.99; H, 3.40; N, 15.74; Mg, 1.70; In, 16.12. Found: C, 26.57; H, 4.04; N, 14.74; Mg, 1.12; In, 16.23.

[13] (a) Dhingra, S.; Kanatzidis, M. G. *Polyhedron* **1991**, *10*, 1069. (b) Kanatzidis, M. G.; Dhingra, S. *Inorg. Chem.* **1989**, *28*, 2026.