Synthesis and Structure of a Bridged Twelve-membered Silver–Zinc–Sulfur Cyclic Compound: a Combination of Hard and Soft Lewis Acidic and Basic Centres

Matthias Steiner, Hansjörg Grützmacher,* Laszlo Zolnai and Gottfried Huttner

Anorganisch Chemisches Institut der Universität, Im Neuenheimer Feld 270, W-6900 Heidelberg, Germany

The reaction of silver trifluoromethanesulfonate **2** with zinc bis[bis(trimethylsilyl)amide] **4** and 2,4,6-triisopropylbenzenethiol **5** in a 4 : 4 : 6 ratio yields the mixed metal thiolate complex **3** with a twelve-membered silver–zinc–sulfur ring bridged by two trifluoromethanesulfonate anions; compound **3** is remarkably stable in solution.

Inspired by the fascinating structures of metal thiolates[1] and recent work by van Koten and his coworkers[2] we started a research programme to study the molecular structures, properties and reactivity of such mixed compounds in which hard and soft Lewis acidic and basic centres are combined in one molecule. For metal thiolates of group 10 (Cu, Ag, Au) and 11 (Zn, Cd, Hg) much less is known about the structures of ternary[3] than of binary thiolates.[1] The first studies on mixed organothiolate metal compounds with soft (Cu^+) and hard (Mg^{2+}) centres are promising.[2c]

Our approach is simple: mixing low-coordinated complexes of hard and soft donor and acceptor centres in a non-coordinating solvent should lead to products in a self-organizing process.[4] Because no extra ligands are added we expect a high reactivity of the resulting complexes. As a first example we report here the synthesis of the mixed silver–zinc thiolate complex **3**. Mixing the low-coordinated zinc thiolate amide complex **1**[5] with silver trifluoromethanesulfonate (triflate) **2** in methylene chloride as solvent affords **3** in good yield (Scheme 1).

Colourless crystals form after several minutes which were suitable for an X-ray diffraction study; results† are shown in Fig. 1. The molecular structure of **3** is based on a twelve-membered centrosymmetric silver–zinc–sulfur ring which is doubly bridged by two CF_3SO_3 anions. The inorganic skeleton is wrapped by the lipophilic 2,4,6-$Pr^i_3C_6H_2$ and CF_3 groups, which make compound **3** moderately soluble in hydrocarbons. Fig. 1 clearly shows the chair conformation of the ring, which is expected for an $(AgSR)_6$ compound[6] in the solid state. In the present case this hexameric binary thiolate is 'diluted' by two zinc atoms. It is not surprising that a complete exchange of ligands occurred. In the cyclic compound **3** the hard Lewis acidic Zn^{2+} centres are bound to two of the hard Lewis basic oxygen atoms [O(5) and O(6)] of the triflate anions while the soft silver cations bind the soft sulfur atoms. The zinc atoms adopt a distorted tetrahedral geometry [S(1)–Zn(1)–S(3a) 135.4(1)°] while the silver atoms have a low coordination number which is not unusual for sterically congested silver thiolates.[1b,c] The silver atoms have weak contacts to the remaining oxygen atoms of the triflate anions [Ag(1)–O(4a) 2.961(2) Å; Ag(2)–O(4a) 3.102(1) Å] which might cause a slight deviation from linearity of the S–Ag–S units [S(1)–Ag(1)–S(2) 173.6(1)°; S(2)–Ag(2)–S(3) 175.7(1)°]. The bond lengths in **3** are in the usual range for compounds with the metal atom in a comparable coordination (Ag–S 2.37–2.40 Å; Zn–S 2.25 Å, Zn–O 2.08 Å). The sum of angles of the pyramidal sulfur atoms S(1), S(2) and S(3) range from 310.7 to 319.8°. Freezing of the inversion process at these sulfur atoms in solution at lower temperatures leads to complex ^1H NMR spectra which were not analysed in detail.

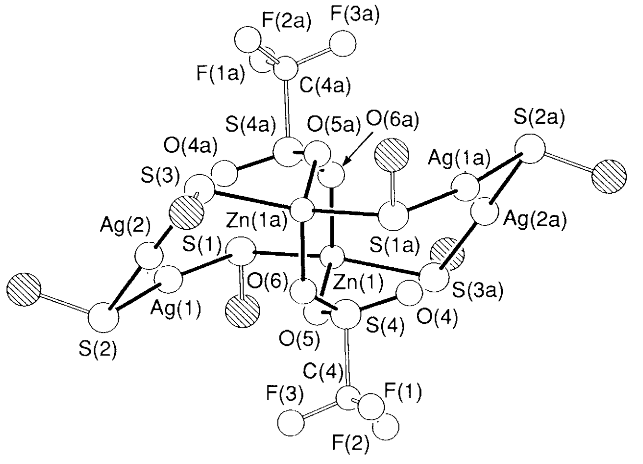
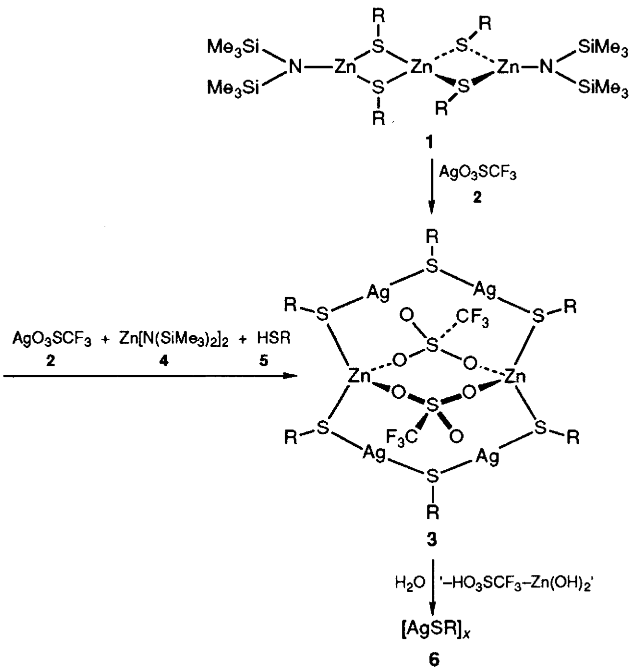


Fig. 1 Oblique view of the molecular structure of **3** showing the chair conformation of the twelve-membered Ag, Zn, S ring and the two bridging CF_3SO_3 anions. Hatched rings correspond to the 2,4,6-$Pr^i_3C_6H_2$ groups. Selected bond length (Å) and angles (°): Ag(1)–S(1) 2.398(1), Ag(1)–S(2) 2.372(1), Ag(2)–S(2) 2.368(1), Ag(2)–S(3) 2.389(1), Zn(1)–S(1) 2.250(1), Zn(1)–S(3a) 2.253(1), Zn(1)–O(5) 2.087(3), Zn(1)–O(6a) 2.080(3), Ag(1)–O(4a) 2.961(2), Ag(2)–O(4a) 3.102(1); S(1)–Ag(1)–S(2) 173.6(1), S(2)–Ag(2)–S(3) 175.7(1), S(1)–Zn(1)–S(3a) 135.4(1), S(1)–Zn(1)–O(5) 108.7(1), S(3a)–Zn(1)–O(6a) 107.3(1), O(5)–Zn(1)–O(6a) 93.2(1); sums of angles: at S(1) 316, S(2) 310.7, 319.8.

More interestingly the formation of **3** is independent of the stoichiometry of the starting materials and **3** may be prepared alternatively from the silver salt **2**, zinc bis[bis(trimethylsilyl-



Scheme 1 R = 2,4,6-$Pr^i_3C_6H_2$

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† **3**: triclinic, space group $P\bar{1}$, a = 11.503(3), b = 14.367(4), c = 17.681(5) Å, α = 103.65(2), β = 101.95(2), γ = 101.45(2)°, V = 2682.27 Å^3, Z = 1, four-circle diffractometer (Mo-Kα radiation, ω scan, $2 \leqslant 2\theta \leqslant 46°$), 7060 measured reflections, 5987 observed [$I > 2\sigma(I)$]. Non-hydrogen atoms anisotropic, hydrogen atoms isotropic, phenyl rings refined as rigid groups; 493 parameters, R = 0.0348, R_w = 0.0305. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

amide)][7] **4** and the thiol **5** in a one-pot procedure.‡ Clearly, compound **3** is indeed formed by self organization of the components of the reaction mixture and is the most thermodynamically stable species in this system. On the basis of the ^{1}H NMR spectra in $CDCl_3$ solution§ **3** is stable up to 70 °C, unexpected for a large molecule of this type. The crosslinking CF_3SO_3 groups are probably mainly responsible for this thermal stability. In air **3** can be handled briefly without decomposition but is moisture-sensitive in solution. The only hydrocarbon-soluble metal-containing product to be formed is the silver thiolate **6**.§ We could not grow crystals of **6** suitable for an X-ray analysis, but its molecular weight (355) in dilute benzene solution (5×10^{-3} mol dm^{-3}) indicates the presence of a monomeric silver thiolate (M 342.9), with complete fragmentation of the thiolate aggregate in solution.

The easy preparation, stability against fragmentation and reasonable solubility of **3** (up to 0.08 mol dm^{-3} in $CHCl_3$ at ambient temperature) makes this and related compounds interesting candidates for studying the reactivity of mixed polymetal thiolates.[2]

We thank Professor Dr Gerhard van Koten for fruitful discussions. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and Dr Otto Röhm Gedächtnisstiftung.

Received, 12th February 1992; Com. 2/00741J

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3 A Literature search in the Crystallographic Data Centre file for structures for mixed Zn, Ag, S or Zn, Cu, S compounds was unsuccessful. Examples for mixed Cu, Ag thiolates are known: *e.g.* G. Henkel, B. Krebs, P. Betz, H. Fietz and K. Saatkamp, *Angew. Chem.*, 1988, **100**, 1373; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1326.

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6 To the best of our knowledge no structure for an $(AgSR)_6$ compound is known, but the structure of the closely related $[AuS(2,4,6\text{-}Pr^{i}{}_3C_6H_2)]_6$ has been reported recently: I. Schröter and J. Strähle, *Chem. Ber.*, 1991, **124**, 2164.

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‡ To AgO_3SCF_3 **2** (5.65 mmol) suspended in dry CH_2Cl_2 (15 ml) where added $Zn[N(SiMe_3)_2]_2$ **4** (5.65 mmol) and 2,4,6-triisopropylbenzenethiol **5** (8.47 mmol). The reaction was slightly exothermic and the mixture became clear. Overnight colourless crystals of **3** (1.7 g, 53% based on **2**) formed; m.p. >250 °C (decomp.). Another 0.8 g (78% combined yield) was isolated from the mother liquor by evaporation *in vacuo* and washing the residue several times with small quantities of toluene.

§ **3**: ^{1}H NMR ($CDCl_3$, 298 K): δ 1.04 (d, $^{3}J_{HH}$ 6.70 Hz), 1.17 (d, $^{3}J_{HH}$ 6.87 Hz), 1.19 (d, $^{3}J_{HH}$ 6.89 Hz), 1.24 (d, $^{3}J_{HH}$ 6.85 Hz) (108 H total, Me); 2.76 (m, 6 H, CH) 3.93 (m, 8 H, CH), 4.31 (m, 4 H, CH), 6.81 (s, 8 H, ArH), 6.85 (s, 4 H, ArH); ^{19}F NMR ($CDCl_3$, 298 K): δ −77.26 (s, CF_3). **6**: m.p. 222 °C (decomp.); ^{1}H NMR ($CDCl_3$, 298 K): δ 1.19 (d, $^{3}J_{HH}$ 6.75 Hz, 12 H, Me), 1.22 (d, $^{3}J_{HH}$ 6.75 Hz, 6 H, Me), 2.83 (septet, $^{3}J_{HH}$ 6.75 Hz, 1 H, CH), 4.20 (septet, $^{3}J_{HH}$ 6.75 Hz, 2 H, CH), 6.93 (s, 2 H, ArH); ^{13}C NMR ($CDCl_3$, 298 K): δ 23.8 (s, Me of *ortho* Pr^{i}), 24.1 (s, Me of *para* Pr^{i}), 32.8 (s, CH of *ortho* Pr^{i}), 34.0 (s, CH of *para* Pr^{i}), 121.7 (s, C-3, C-5), 127.8 (s, C-1), 146.1 (s, C-4), 149.3 (s, C-2, C-6).