# Molecular Mercury Zinc Sulfides

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*Dedicated to Professor Dieter Fenske on the occasion of his 60th birthday*

**Keywords:** Mercury / Zinc / S ligands / Tripod ligands

Reactions between $Tp^{Ph,Me}$Zn-SH and mercury bis(trimethylsilyl)amides yield the monomeric complexes $Tp^{Ph,Me}$-Zn–S–$HgCH_2Ph$ (**1**) and $Tp^{Ph,Me}$Zn–S–Hg–S–Zn$Tp^{Ph,Me}$ (**2**). The bent Zn–S–Hg and linear S–Hg–S arrays in these molecular metal sulfides were confirmed by structure determinations.

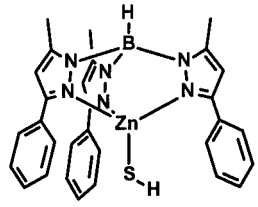

## Introduction

The most characteristic feature of sulfur as a ligand in metal complexes is its tendency to be three- or four-coordinate by bridging several metal atoms. This has long been known for classical[1] as well as for organometallic[2] coordination chemistry. In recent years Fenske and co-workers have provided impressive examples of high-nuclearity clusters constructed by the nucleation of metal ions around sulfide ions.[3−5]

In contrast, transition metal complexes containing conventional divalent sulfur in monomeric M−S−M arrays are rare. Outside the field of plain thiometalates[6] there are only scattered examples in the literature.[7] Among the few complexes in which two metals are linked by nothing but a sulfide ligand are $[Cp(CO)_3W]_2S$,[8] $[(Ph_3P)Au]_2S$[9] and $[(triphos)Ni]_2S^{2+}$.[10] As a rule the high inertness of the $L_nM$ units contained in these complexes has rendered their metal centers M inaccessible to aggregation triggered by loss of their ligands L.

Our present work in this field, after past experiences with polynuclear organometallic complexes,[2] results from our attempts to construct monofunctional zinc complexes for biomimetic and catalytic studies. Since sulfur ligation of zinc is a common feature of both industrially applied and biological zinc species, we have also experimented with thiolates and sulfide as ligands for zinc. Like others we experienced aggregation of the complexes[11−13] and nucleation around sulfide in the complex cores.[14,15] However, by using bulky pyrazolylborate ligands we also learnt to protect the zinc ions by encapsulation. This way zinc-hydrosulfide complexes became accessible as the very stable and versatile Tp*Zn−SH species,[16] and we could prepare $Tp^{Cum,Me}$Zn−S−Zn$Tp^{Cum,Me}$ as the first molecular zinc sulfide.[17]

After exploiting the basic chemistry of the Zn−SH function[16] we have started using the Tp*Zn−SH units as building blocks for new complexes. The present paper describes the application of $Tp^{Ph,Me}$Zn−SH for the preparation of two molecular mercury zinc sulfides.




$Tp^{Ph,Me}$Zn–SH

## Results and Discussion

### Preparations

The most straightforward way of utilizing the Tp*Zn−S moiety for preparative purposes would be the deprotonation of Tp*Zn−SH. It turned out, however, that the "thiolates" Tp*Zn−$S^-$ are not stable enough for this purpose.[16] Therefore we resorted to the implicit deprotonation approach, which consists in the reaction between a thiol and a metal bis(trimethylsilyl)amide. In this approach the metal-bound amide is the base for deprotonation and at the same time the ligand being substituted by the thiolate. We have used this method before for the synthesis of otherwise inaccessible zinc thiolates,[18] and we now applied it to the corresponding mercury amides.

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The reaction between $Tp^{Ph,Me}Zn-SH$ and benzylmercury bis(trimethylsilyl)amide yielded the Zn−S−Hg complex **1**. Likewise $Tp^{Ph,Me}Zn-SH$ and mercury bis[bis(trimethylsilyl)amide] produced the Zn−S−Hg−S−Zn complex **2**. Both reactions resulted in air-stable colourless crystalline compounds in reasonable yields. While their IR data are uninformative, their $^1H$ NMR spectra (see Exp. Sect.) prove the presence of the Tp and Bz ligands. Compounds **1** and **2** are the first fully characterized mixed-metal sulfide complexes of the second subgroup. Mixed-metal sulfide clusters containing zinc and cadmium have been described but not isolated in a pure form.[19,20]

$Tp^{Ph,Me}Zn\text{-}S\text{-}HgCH_2Ph$
**1**
$Tp^{Ph,Me}Zn\text{-}S\text{-}Hg\text{-}S\text{-}ZnTp^{Ph,Me}$
**2**

### Structures

Complex **1** (see Figure 1) contains a nearly right-angled Zn−S−Hg array. Its two constituents, the Tp*ZnS unit and the BzHgS unit, are quite normal with typical Zn−S, Hg−S and Hg−C bond lengths. Reference compounds are the Tp*Zn−SH complexes themselves[16] and the organomercury thiolates.[21] As expected for two-coordinate mercury, the S−Hg−C array is very close to being linear. The dihedral angle defined by the Zn−S and C−C bonds with respect to the Zn−S−Hg axis is 174°.

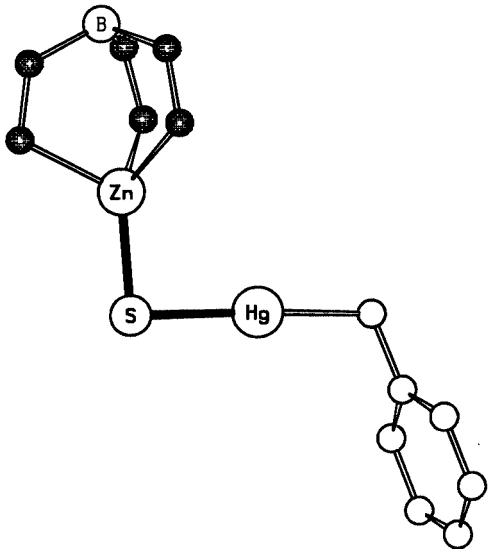


Figure 1. Molecular structure of complex **1** (for reasons of clarity the pyrazolylborate ligand is reduced to its $BN_6$ skeleton); important bond lengths (Å) and angles (°): Zn−N 2.065−2.092(5), Zn−S 2.221(2), Hg−S 2.316(2), Hg−C 2.115(1); Zn−S−Hg 93.41(7), S−Hg−C 176.3(5)

Complex **2** (see Figure 2) is centered around a nearly linear S−Hg−S array with Hg−S distances very similar to those in **1**. The two Hg−S−Zn angles are larger than the one in **1** and differ by 12°, probably due to steric congestion. The two Tp*Zn−S units are practically superimposable with that in **1**. While in **1** the Hg−S−Zn and Hg−C−C units define a trans array, the corresponding two Hg−S−Zn units in **2** are gauche, their dihedral angle being 95°. Complex **2** can be compared with monomeric mercury bis(thiolates), whose structures in the solid state range from linear two-coordinate to polymers with four- and five-coordinate mercury.[22] Furthermore the Zn−S−Hg−S−Zn sequence in **2** is analogous to the 1D polymeric array of mercury and sulfur in cinnabar, the thermodynamically more stable modification of HgS.[23] In cinnabar the Hg−S bond lengths are 2.37 Å and the dihedral angle is 93°.

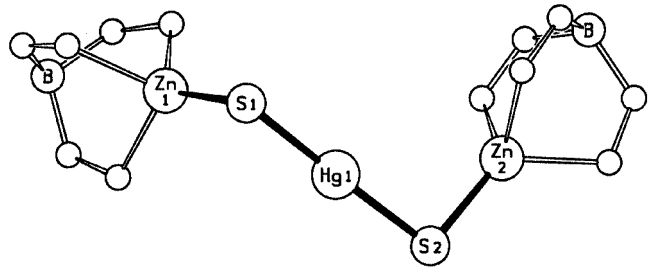


Figure 2. Molecular structure of complex **2** (for reasons of clarity the pyrazolylborate ligands are reduced to their $BN_6$ skeletons); important bond lengths (Å) and angles (°): Zn−N 2.070−2.086(3), Zn1−S1 2.226(1), Zn2−S2 2.219(1), Hg−S1 2.299(1), Hg−S2 2.303(1); Zn1−S1−Hg 108.70(5), Zn2−S2−Hg 96.75(5)

## Conclusions

The facile preparations of **1** and **2** have proved the suitability of the $Tp^*ZnS^-$ unit for the construction of molecular metal sulfides. Except for our Tp*Zn−S−ZnTp* [17] no such sulfides of zinc, cadmium or mercury with simple M−S−M arrays seem to have been reported, even though the standard arrangements of the types $M_3(\mu_3\text{-}S)$ and $M(\mu\text{-}S)_2M'$ are known for heterometallic mercury complexes.[24,25] Furthermore, the chain-like array of three metal and two sulfur atoms in **2** seems to be unprecedented in coordination chemistry, although the relation to cinnabar makes it understandable that it exists in complex **2**. The tendency of mercury to have a linear twofold coordination and the highly covalent nature of the mercury-ligand bonds may be important for the stabilization of these molecular metal sulfides. We believe, however, that the protection by the encapsulating Tp* ligands will stabilize similar complexes with other metals too.

## Experimental Section

**General:** For general working and measuring procedures, see ref.[26] All reactions were performed under an inert atmosphere. $Tp^{Ph,Me}Zn-SH$[16] and the mercury silylamides[27] were prepared according to the published procedures.

**Complex 1:** $BzHgN(SiMe_3)_2$ (163 mg, 0.36 mmol) and $Tp^{Ph,Me}Zn-SH$ (210 mg, 0.36 mmol) in 20 mL of dichloromethane were stirred for 2 h. After removal of all volatiles in vacuo the residue was recrystallized from acetonitrile, yielding 179 mg (57%) of

Table 1. Crystallographic data

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{37}H_{35}BHgN_6SZn$ ·$CH_3CN$ | $C_{60}H_{56}B_2HgN_{12}S_2Zn_2$ ·$2CH_3CN$ |
| Molecular mass | 872.6 + 41.0 | 1362.3 + 82.0 |
| Crystal size [mm] | 0.3 × 0.3 × 0.2 | 0.3 × 0.3 × 0.2 |
| Space group | $P2_1/n$ | $P\bar{1}$ |
| Z | 4 | 2 |
| *a* [Å] | 11.630(2) | 13.501(3) |
| *b* [Å] | 20.590(4) | 14.077(3) |
| *c* [Å] | 15.350(3) | 17.529(4) |
| α [°] | 90 | 101.44(3) |
| β[°] | 96.27(3) | 99.32(3) |
| γ [°] | 90 | 102.91(3) |
| *V* [Å$^3$] | 3654(1) | 3108(1) |
| d(calc) [gcm$^{-3}$] | 1.66 | 1.54 |
| μ(Mo-$K_\alpha$) [mm$^{-1}$] | 4.95 | 3.35 |
| hkl range | *h*: −14 to 9<br>*k*: −25 to 25<br>*l*: −16 to 18 | *h*: −16 to 16<br>*k*: −16 to 16<br>*l*: 0 to 21 |
| Measured reflections | 14342 | 11318 |
| Independent reflections | 6705 | 11318 |
| Observed refl. [$I > 2\sigma(I)$] | 5764 | 10121 |
| Parameters | 451 | 766 |
| Refined reflections | 6705 | 11318 |
| $R_1$ (obs.refl.) | 0.073 | 0.041 |
| $wR_2$ (all refl.) | 0.209 | 0.101 |
| Residual electron density [e/ Å$^3$] | +2.8/−4.5 | +2.9/−3.0 |

**1** as colorless crystals which turned to a powder upon drying in vacuo, M.p. 202 °C (dec.). $C_{37}H_{35}BHgN_6SZn$ (872.6): calcd. C 50.33, H 4.04, N 9.63; found C 50.73, H 4.03, N 9.61. $^1$H NMR ($CDCl_3$): δ = 1.76 (s, 2 H, $CH_2$), 2.56 [s, 9 H, Me(pz)], 6.17 [s, 3 H, H(pz)], 6.69 (m, 2 H, Bz), 6.89 (m, 1 H, Bz), 7.06 (m, 2 H, Bz), 7.30 (m, 9 H, Ph), 7.61 (m, 6 H, Ph) ppm.

**Complex 2:** $Tp^{Ph,Me}Zn-SH$ (500 mg, 0.86 mmol) and $Hg[N(SiMe_3)_2]_2$ (224 mg, 0.43 mmol) in 30 mL of dichloromethane were stirred for 15 min, upon which the solution turned black. After removal of all volatiles in vacuo the residue was taken up in a minimum amount of hot acetonitrile, filtered hot and the filtrate kept at room temp. for one day. 210 mg (36%) of **2** were precipitated as colorless crystals, which turned to a powder upon drying in vacuo. M.p. 248 °C (dec.). $C_{60}H_{56}B_2HgN_{12}S_2Zn_2$ (1362.3): calcd. C 52.90, H 4.14, N 12.34; found C 52.72, H 4.20, N 12.42. $^1$H NMR ($CDCl_3$): δ = 2.55 [s, 18 H, Me(pz)], 6.12 [s, 6 H, H(pz)], 7.04 (m, 18 H, Ph), 7.48 (m, 12 H, Ph).

**Structure Determinations:**[28] Crystals of **1** and **2** were obtained from the reaction mixtures. Diffraction data were recorded at room temp. with the ω/2θ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (Mo-$K_\alpha$, λ = 0.7107 Å) and a graphite monochromator and subjected to empirical absorption corrections. The structures were solved by direct methods and refined anisotropically with the SHELX program suite.[29] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5-times those of their attached atoms. Parameters were refined against $F^2$. The R values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]\Sigma[w(F_0^2)^2]]^{1/2}$. Drawings were produced with SCHAKAL.[30] Table 1 lists the crystallographic data.

## Acknowledgments

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