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Controlled Formation of Tri- and Octanuclear Benzylthiolate Complexes of Zinc

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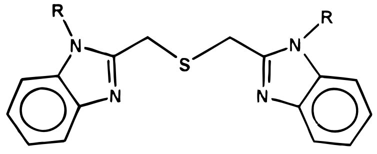
The tendency of transition metal thiolates, specifically those of zinc, to form oligomeric and polymeric species is well-established.[1−3] In order for their nuclearity to be reduced, the measures of using sterically demanding thiolates[4] or of adding appropriate counterions[5] have been taken successfully in several cases. The application of coligands containing heterocyclic nitrogen donors has led to stable mononuclear complexes with the highly preferred ZnN_2S_2 environment.[6] The large majority of zinc thiolate complexes described so far contain aromatic thiolates. Aliphatic thiolates either are constituents of oligonuclear species or are stabilized in ZnN_2S_2 complexes as parts of chelating (N,S) ligands. Typically the coordination patterns $[Zn(SR)_4]^{2-}$ or $[L_2Zn(SR)_2]$, which are the ones used by nature for "structural zinc" in protein environments (L = histidine, i.e., a heterocyclic nitrogen donor; SR = cysteinate, i.e., an aliphatic thiolate),[7] have not been obtained yet in the form of simple coordination compounds with monodentate L and aliphatic SR.

We have contributed to this field by the stabilization of monodentate thiolates (including aliphatic ones) with encapsulating tripodal ligands,[8] the construction of trigonal-bipyramidal ZnN_3S_2 complexes,[9] the use of chelating (N,S) ligands to obtain thiolate-bridged oligonuclear species,[10] and the application of sterically demanding (N,N) chelate ligands to stabilize (L-L)-$Zn(SR)_2$ compounds with aliphatic thiolates including cysteinyl peptides.[11] In the latter project we observed that the substituent pattern of the (L-L) ligands exerts subtle control over the isolability of (L-L)$Zn(SR)_2$ species with aliphatic thiolates. For instance these species could not be obtained for (L-L) = *o*-phenanthroline, but were isolable for its 2,9-dimethyl derivative neocuproin. Similarly, of the R-BIMS ligands, the one with R = propyl stabilizes aliphatic (L-L)$Zn(SR)_2$, but the one with R = methyl does not.[11b] This induced us to screen the R-BIMS ligands and the thiolates to find out about the stability range of mononuclear complexes and about alternative compositions. This paper reports our observations for the benzylthiolate system.



Me-BIMS: R = CH_3
Pr-BIMS: R = $CH_2CH_2CH_3$
Bz-BIMS: R = CH_2Ph

Experimental Section

The general experimental techniques were as described previously.[12] All manipulations were done in an inert atmosphere and using solvents which were degassed and saturated with nitrogen by several cycles of evacuation and flooding with nitrogen. The ligand Me-BIMS was prepared according to the published procedure.[13] The spectroscopic and analytical characterization of the new complexes is given in the Supporting Information.

Preparations. $[Zn_3(Me\text{-}BIMS)(SBz)_6]$ (1). A solution of benzyl mercaptan (112 mg, 0.90 mmol) in methanol (150 mL) was treated with sodium methoxide (3.8 mL (0.90 mmol) of a 0.24 M methanol solution). Then $Zn(NO_3)_2 \cdot 4H_2O$ (134 mg, 0.45 mmol) in methanol (50 mL) was added with vigorous stirring over a period of 1 h. Me-BIMS (145 mg, 0.45 mmol), dissolved in 20 mL of boiling methanol, was added, and the clear solution was stirred for 1 h. After the volume was reduced to 25 mL in vacuo, the solution was allowed to stand. Within 1 week a colorless precipitate had formed, which was filtered off, washed with a few milliliters of ice-cold methanol, and dried in vacuo. Recrystallization from hot acetonitrile (20 mL) yielded 85 mg (45%) of **1** as colorless crystals, mp 134 °C dec, which were dried in vacuo for several hours to remove all solvent of crystallization.

$[BzEt_3N]_2[Zn_8(S)(SBz)_{16}]$ (2). Sodium methoxide (21.3 mL (4.25 mmol) of a 0.20 M methanol solution) and benzyl mercaptan (528 mg, 4.25 mmol) were combined in methanol (75 mL). Then $Zn(NO_3)_2 \cdot 4H_2O$ (421 mg, 1.42 mmol) in methanol (50 mL) was added with vigorous stirring over a period of 2 h. Finally a solution of $[BzEt_3N]Cl$ (323 mg, 1.42 mmol) in methanol (20 mL) was added. The clear solution was slowly reduced to 30 mL in vacuo in a warm water bath, filtered through a fine-porosity frit, and left to stand under an inert atmosphere. Over a period of 4 weeks the solution slowly turned yellow and formed a partly crystalline precipitate. This was filtered off, washed with a few milliliters of ice-cold methanol, and dried in vacuo for an extended period, leaving behind 392 mg (76%) of solvent-free colorless **2**, mp 136 °C dec.

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Table 1. Crystallographic Details

	1	**2**
formula	$C_{60}H_{60}N_4S_7Zn_3 \cdot 2CH_3CN$	$C_{138}H_{156}N_2S_{17}Zn_8 \cdot 5CH_3OH$
mol wt	1339.76	3071.22
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
a (Å)	13.550(2)	16.739(3)
b (Å)	15.313(2)	16.762(3)
c (Å)	15.493(3)	28.154(6)
α (deg)	90.25(2)	106.82(3)
β (deg)	91.87(2)	100.11(3)
γ (deg)	95.68(2)	91.14(3)
V (Å^3)	3197(1)	7423(3)
d_{calc} (g cm^{-3})	1.39	1.37
μ(Mo Kα) (mm^{-1})	1.39	1.56
R1 (obs reflns)[a]	0.074	0.050
wR2 (all reflns)[b]	0.265	0.137

[a] $R1 = \sum|F_o - F_c|/\sum F_o$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Structure Determinations. Crystals of both compounds were taken from the reaction products before drying in vacuo and sealed in glass capillaries to avoid loss of solvent of crystallization. Diffraction data were recorded with the image plate technique on a Stoe IPDS diffractometer fitted with a molybdenum tube (Kα, $\lambda = 0.7107$ Å) and a graphite monochromator. No absorption corrections were applied. The structures were solved with direct methods and refined anisotropically with the SHELX program suite.[14] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Parameters were refined against F^2. Drawings were produced with SCHAKAL.[15] Table 1 lists the crystallographic data.

Results and Discussion

We had observed previously[11b] that of the R-BIMS ligands those with R = propyl and R = benzyl allow the formation of the complexes (R-BIMS)Zn(SBz)$_2$ with the standard tetrahedral ZnN_2S_2 coordination pattern. Combining the reagents NaSBz, Zn(ClO$_4$)$_2$, and Me-BIMS had originally produced an intractable, probably polymeric, precipitate. Changing the conditions, mainly by adding Zn(NO$_3$)$_2$ very slowly, has now allowed the isolation of trinuclear **1** in a reasonable yield. **1** represents a compromise between the polymerization tendency of Zn(SBz)$_2$ and the confinement to mononuclearity brought about by the donor quality and steric requirements of the chelate ligand. There seems to be a delicate balance of these two forces, as complexes like **1** were obtained neither with other R-BIMS ligands nor with other thiolates.

Zn_3(Me-BIMS)(SBz)$_6$
1

During the preparation of **1**, NaSBz and Zn(NO$_3$)$_2$ are combined first, producing a clear solution, presumed to contain solvated monomeric Zn(SBz)$_2$ and anionic thiolatozincates of varying nuclearity. We made various attempts to isolate one of these compounds in a crystalline form. During these attempts we observed that in a period of weeks and in the presence of alkylammonium cations a chemical change occurs which shows up in a color change of the solution to yellow. In the presence of benzyltriethylammonium chloride, compound **2** precipitated from the solution. **2** contains sulfide, which was not present in the initial reaction solution and which cannot have formed from benzylthiolate by oxidation, as air was carefully excluded and nitrate has never been observed by us to oxidize thiols or thiolates under these conditions. The formation of sulfide has also been observed by Dance in solutions containing thiolates and alkylammonium ions and has tentatively been explained by alkyl or aryl transfer,[16] and the loss of sulfide from benzylthiols due to the relative stability of benzyl cations is known from organic chemistry.[17] The sulfide ions seem to be necessary as a nucleus around which an octameric unit of Zn(SBz)$_2$ can assemble. The yield of compound **2** is quite good and reproducible, indicating that its composition is highly favored in the presence of sulfide. Addition of sulfide to the fresh reaction mixture, however, produced precipitates whose compositions were variable and not identical to those of **2**.

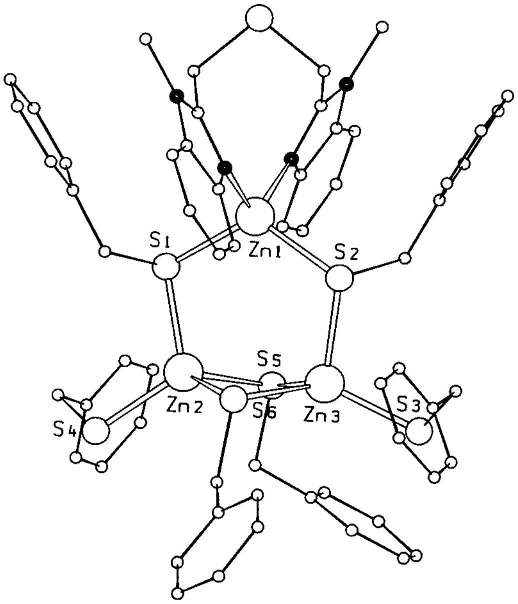

Figure 1. Molecular structure of Zn$_3$(Me-BIMS)(SBz)$_6$ (**1**).

Table 2. Selected Atomic Distances in Complex **1** (Å)

Zn1···Zn2	3.780(2)	Zn2−S1	2.359(3)
Zn1···Zn3	3.958(2)	Zn3−S2	2.382(3)
Zn2···Zn3	3.069(2)	Zn2−S4	2.273(4)
Zn1−N1	2.026(9)	Zn3−S3	2.264(4)
Zn1−N2	1.993(9)	Zn2−S5	2.388(4)
Zn1−S1	2.324(3)	Zn3−S5	2.389(4)
Zn1−S2	2.319(3)	Zn2−S6	2.397(4)
		Zn3−S6	2.403(4)

[BzEt$_3$N]$_2$[Zn$_8$(S)(SBz)$_{16}$]
2

The compositions and constitutions of **1** and **2** became clear only after the structure determinations. Figure 1 and Table 2 give the result for **1**. The three zinc ions form an isosceles triangle, and their coordination is tetrahedral to a good approximation. The zinc−sulfur distances fall into three categories, those to terminal thiolate being the shortest and those from Zn2 and Zn3 to the bridging thiolates being the longest. The Cambridge Crystallographie Data File contains no entry on a $L_2M_3(ER)_6$ complex like **1** for any metal or any chalcogen yet. So far the structures of two other trinuclear zinc−thiolate complexes have been described. $Zn_3(CH_2SiMe_3)_3(SC_6H_2i\text{Pr}_3)_3$[18] and Zn$_3$(*o*-phen)$_2$(toluene-3,4-dithiolate)$_3$[19] have little similarity

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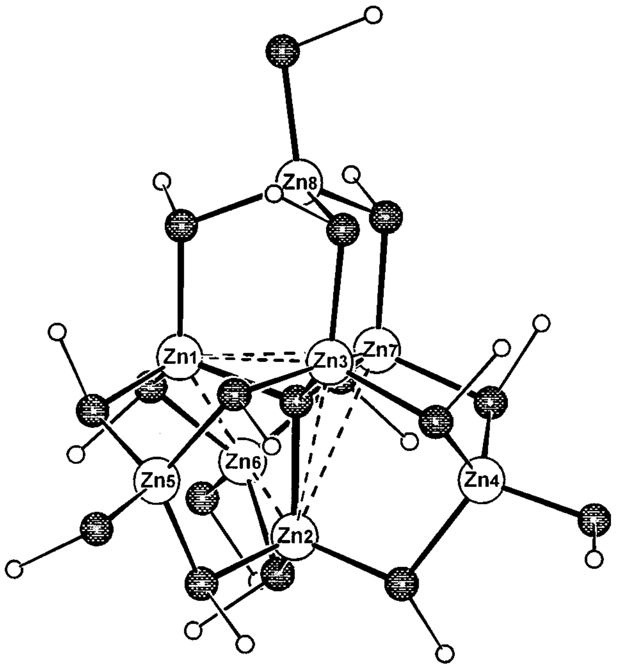

Figure 2. Structure of the anion of $[BzEt_3N]_2[Zn_8(S)(SBz_{16})]$ (**2**) (central SZn_4 tetrahedron outlined by dashed lines, sulfur atoms shaded, phenyl rings omitted).

with **1**, however. But fragments of **1** can be compared with known zinc complexes. Thus the (Me-BIMS)Zn(SBz)$_2$ part of **1** represents quite a normal ZnN_2S_2 complex, immediately comparable with the mononuclear (R-BIMS)Zn(SR)$_2$ complexes,[11b] and the $Zn_2(SBz)_6$ part of **1** corresponds to the $Zn_2(SR)_6^{2-}$ units with R = Et[5b] or R = Ph[20] and with R = cysteinate in the GAL4 transcription factor.[21]

The octanuclear anion of compound **2** (see Figure 2) displays a central SZn_4 unit which is capped on all four faces by ZnS_4 units. All zinc ions are surrounded by four sulfur atoms in an approximately tetrahedral arrangement. The 32 zinc−sulfur distances range from 2.15 to 2.56 Å with no systematic distributions, as evidenced by Table 3. The literature contains structure determinations of three complexes with a $M_8(E)X_{16}$ arrangement, namely, $[NMe_4][Zn_8(Cl)(SPh)_{16}]$[16] and $[NEt_4]_2[Cd_8(S)(SePh)_{16}]$ by Dance[22] and two structures of salts of $[Cd_8(S)(SPh)_{12}Cl_4]^{2-}$ by Tang.[23] Unlike **2**, all three show very little variation in their M−E and M−X bond lengths. Other reported $M_8E_x(ER)_y$ complexes such as $Gd_8S_6(SPh)_{12}(THF)_8$[24] and $Sm_8Se_6(SePh)_{12}(THF)_8$[25] contain a cubelike arrangement of the eight metal ions.

Table 3. Zinc−Sulfur Distances in Complex **2** (Å)

(a) Central Sulfide			
Zn1−S	2.305(2)	Zn3−S	2.557(2)
Zn2−S	2.429(2)	Zn7−S	2.186(2)
(b) Inner Zn_4 Unit			
Zn1−S(Zn5)	2.182(2)	Zn3−S(Zn4)	2.320(2)
Zn1−S(Zn6)	2.534(2)	Zn3−S(Zn5)	2.148(2)
Zn1−S(Zn8)	2.430(2)	Zn3−S(Zn8)	2.413(2)
Zn2−S(Zn4)	2.338(2)	Zn7−S(Zn4)	2.310(2)
Zn2−S(Zn5)	2.171(2)	Zn7−S(Zn6)	2.528(2)
Zn2−S(Zn6)	2.528(2)	Zn7−S(Zn8)	2.434(2)
(c) Peripheral Zn (Bridging)			
Zn4−S(Zn2)	2.358(2)	Zn6−S(Zn1)	2.304(2)
Zn4−S(Zn3)	2.413(2)	Zn6−S(Zn2)	2.379(2)
Zn4−S(Zn7)	2.344(2)	Zn6−S(Zn7)	2.302(2)
Zn5−S(Zn1)	2.385(2)	Zn8−S(Zn1)	2.333(2)
Zn5−S(Zn2)	2.427(2)	Zn8−S(Zn3)	2.400(2)
Zn5−S(Zn3)	2.491(2)	Zn8−S(Zn7)	2.245(2)
(d) Outer Terminal Thiolates			
Zn4−S	2.215(2)	Zn6−S	2.476(2)
Zn5−S	2.174(2)	Zn8−S	2.363(2)

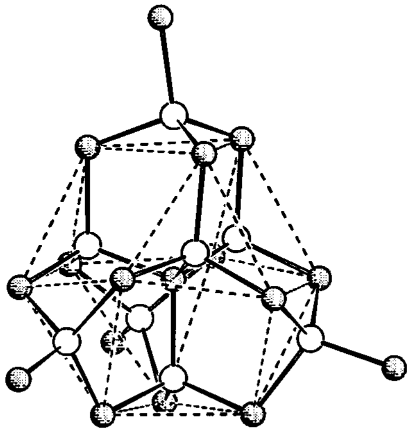

Figure 3. The Zn_8S_{17} core of **2** (viewing direction as in Figure 2, sulfur atoms shaded, cuboctahedral arrangement of the 12 bridging thiolate sulfur atoms indicated by dashed lines).

Polynuclear metal thiolates are often displayed as sections of the corresponding metal sulfide (e.g., zinc blende),[1,2] as evidenced in an aesthetically very pleasing way by $[Zn_{10}S_4(SPh)_{16}]^{4-}$ [26] and $Cd_{32}S_{14}(SPh)_{36}$.[27] This cannot be done for compound **2** and its $M_8(E)X_{16}$ analogues.[16,22,23] Their SZn_4 core is ZnS-like, but the face capping of the SZn_4 unit by the four external ZnS_4 units generates an arrangement of Zn and S which is unlike those around a SZn_4 center in cubic or hexagonal ZnS. However, limiting the discussion to the twelve μ_2 sulfur atoms reveals a spatial arrangement which does conform to that in zinc sulfide. Figure 3 shows that they span a cuboctahedron around the central sulfur atom, which is the pattern of cubic close packing. Thus the location of the zinc and sulfur atoms in the inner Zn_4S_{13} shell of **2** is that of zinc blende. Thereby **2** differs from its $M_8(E)X_{16}$ analogues[16,22,23] which display an icosahedral arrangement of the 12 μ_2 sulfur or selenium atoms.

The question of why the spontaneous aggregation of the species X^{n-}, ER^-, and M^{2+} leads to just the $[XM_8(ER)_{16}]^{n-}$ composition in **2** and its analogues has not been asked yet. We found an answer to this kind of question for the compound $[Zn_7(2\text{-pyridylmethanolate})_{12}]Cl_2$ in the stacking of the aromatic rings creating a symmetrically and completely covered surface of the globular complex cation.[28] This explanation does not work for **2**. Space-filling plots (of which one example is given in the

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Supporting Information) show that the complex anion is not of globular shape nor are its zinc and sulfur constituents hidden under a well-stacked coverage of aromatic rings. Thus it seems to us that, once the central XM_4 core is assembled and there is no excess of X^{n-}, the ER^- and M^{2+} ions in solution can only be attached to this core in the observed way, the reason for this being the preferred tetrahedral coordination of M^{2+}. It remains open whether thermodynamic stability or low solubility allows the observed composition to be isolated rather than any other $M_x(ER)_y$ composition.

Conclusions

The preferred composition and spontaneous formation of **1** and **2** are proven by the fact that both result reproducibly and in good yields from solutions whose compositions are different from those of the products. Obviously the aggregation of the zinc−benzylthiolate entities is controlled by the coligands which act as nucleation starters. When the coligand is a spatially demanding (N,N) chelator, the products are monomolecular $Zn(SR)_2$ complexes.[11] Coligand Me-BIMS is a unique borderline case, allowing the combination of one ligated and two unligated $Zn(SR)_2$ units in the neutral complex **1**. Slow delivery of sulfide allows the growth of the octanuclear anions around the central SZn_4 core. Compounds like **1** and **2** could only be obtained by us with benzylthiolate. In contrast, all previously reported $Zn_x(S)_y(SR)_z$ complexes were of the arylthiolate type. Obviously the aggregation tendency of benzylthiolate, halfway between those of the aliphatic and aromatic thiolates, is, besides the nature of the coligands, the second decisive factor for the observed assemblies.

The $M_3L_2(SR)_6$ composition and structure of **1** seems to be without precedent in coordination chemistry, and we are not aware of any other reported $[M_8(S)(SR)_{16}]^{2-}$ complex. The anion $[Zn_8(S)(SBz)_{16}]^{2-}$ also represents a new structural type for oligonuclear metal thiolates. Its cuboctahedral array of the bridging thiolate sulfur atoms around the central sufide constitutes a S_{13} unit corresponding to the first coordination shell in a cubic close-packed lattice. Altogether compounds **1** and **2** are two more examples of the growing group of complexes between small molecular entities and extended lattice species.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. We thank Prof. D. Fenske and coworkers for obtaining the X-ray data set for **2**.

Supporting Information Available: Spectroscopic and analytical characterization of and fully labeled ORTEP plots for **1** and **2** and one space-filling plot for **2** (4 pages). Two crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

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